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Evaluation of Some Organic Inhibitors for Stainless Steel Corrosion Using Different Electrochemical and Surface Techniques

Maryam Hassan Saeed Al-Hassan

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Evaluation of Some Organic Inhibitors for Stainless Steel Corrosion Using Different Electrochemical and Surface Techniques

A Thesis Submitted to

The Deanship of Graduate Studies of the United Arab Emirates University

By

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In Partial Fulfillment of the degree of

MSc

In

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Acknowledgement

To those whom I hold respect, to the people who where behind me and gave me their support. To all of them I would like to say many thanks to you. Because without your help and support I would not been able to finish this study.

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Finally, I am grateful to my family and friends for standing with me and for their great support and advices.
Abstract

Stainless steels have been extensively used in automotive, industrial, electronics, etc., applications. Iron (Fe) and chromium (Cr) are the main elements with weight percentage contribution of 60-75% and 10-25% respectively. Other elements, such as Ni, Co, Mo, Mn, C etc. are also present with variable concentrations. The purpose of this work is to use different electrochemical and surface techniques to study the corrosion behavior of stainless steel type 316 (percent composition of different chemical elements are listed in table 1) in acid media in presence and absence of different thiophene derivatives (list of inhibitors in figure1). Moreover, other important goals were to study the effect of adding chloride ion to the acidic media on the corrosion behavior of stainless steel, protection efficiency of inhibitors studied, and to determine the temperature coefficient and the adsorption isotherm of the inhibitor on the stainless steel type 316.

Electrochemical techniques such as potentiodynamic polarization, Tafel experiments, polarization resistance and electrochemical spectroscopy were used to evaluate the effect of the inhibitors on the corrosion of stainless steel type 316. Surface analyses were employed to study the surface morphology and structural analysis of the surface using
scanning electron microscope (SEM), Fourier Transform infrared (FT-IR), and x-ray diffraction techniques EDAX.

The results showed distinct effects for the different inhibitors used that depend on the molecular structure and the electron density on the sulfur atom of the thiophene ring. The order of inhibition efficiency was 2-thiophene carboxylic hydrazide > 2-thiophene carboxylic acid > 3-thiophene carboxaldehyde > 2-acetyl thiophene. It was concluded that the inhibitors studied were of the mixed type.

The adsorption pattern for the inhibitors at the stainless steel surface followed a Langmuir isotherm model. The thermodynamic parameters of adsorption were calculated. It was concluded that a thin layer of inhibitor is formed at the surface of steel preventing the corrosion of the specimen in the acid medium. It was also suggested that anchoring of the sulfur atom of the thiophene ring to the surface of the stainless steel takes place that allowed a blanket of the inhibitor molecule to cover the surface.

Surface reflectance FT-IR proved the adsorption of the inhibitor molecule at the stainless steel surface. Scanning electron microscopy showed that the presence of inhibitor protected the surface of the stainless steel against pitting in chloride-containing sulfuric acid electrolyte.
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**List of Abbreviations and Symbols**

- $i_{corr}$  
  Corrosion current

- $E_{corr}$  
  Corrosion potential

- $\Delta E$  
  Change in potential

- $\Delta i$  
  Change in current

- PZC  
  Potential of zero charge

- SHAB  
  Soft and hard acids and bases

- UV  
  Ultra-violet

- AISI  
  American Iron and Steel Institute

- $C_{dl}$  
  Double layer capacitance

- $R_t$  
  Charge transfer resistance

- AC  
  Alternative current

- $E_{pit}$  
  Pitting potential

- SCC  
  Stress corrosion cracking

- $\beta_c$  
  Cathodic Tafel slope

- $\beta_a$  
  Anodic Tafel slope

- E.W  
  Equivalent weight of the corroding species, g.

- TCH  
  2-Thiophene Carboxylic Hydrazide

- TCA  
  2-Thiophene Carboxylic Acid

- TCAL  
  3-Thiophene Carboxaldehyde

- AcT  
  2-Acetyl Thiophene
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- TCAL  
  3-Thiophene Carboxaldehyde

- AcT  
  2-Acetyl Thiophene
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<td>$\theta$</td>
<td>Degree of coverage</td>
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<td>$Q$</td>
<td>Heat of adsorption</td>
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<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
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<td>$z$</td>
<td>Charge of the species</td>
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<td>$F$</td>
<td>Faraday constant</td>
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INTRODUCTION
INTRODUCTION
1. General Introduction

The field of corrosion has seen a tremendous amount of research and development stimulated by problems related to great advances in technology and facilitated by parallel advances in techniques for investigating corrosion problems.

On the other hand, corrosion is an electrochemical process that, lead to the deterioration of a metal or alloy as a result of exposure to and reaction with its environment [1]. Therefore, the use of electrochemical techniques to study the corrosion behavior of stainless steels has been increased considerably in the last two decades. This has lead to improving the ability to predict, by short-term laboratory tests, the behavior and deterioration of stainless steel in different environments.

Stainless steels have a technological and economic importance [2]. Stainless steels are iron alloys containing a minimum of approximately 11% chromium. This amount of chromium prevents the formation of rust in "unpolluted" atmospheric environments [3]. Nowadays, there are more than 190 different kinds of alloys that can be recognized as belonging to the stainless steel family. In some steels chromium content approaches 30% and many other elements are added to provide specific properties. For example, nickel and molybdenum are added for corrosion resistance, carbon, molybdenum, titanium, aluminum, and copper for strength, sulfur and selenium for machinability, and nickel for formability
and toughness. The austenitic stainless steel type 304 has a predominant ranking among all types of steels in terms of yearly produced amount. From corrosion resistance viewpoint, of interest is the low-carbon grades: types 304L, 316L, and 317L. In these grades, the carbon content is reduced to 0.03% to improve resistance to sensitization. Figure 1 illustrates the compositional and property linkages in the stainless steel family of alloys [4].

Stainless steels are used in a wide variety of services in which primary considerations are long service life (in a given environmental condition), reliability, appearance, and sanitary factors. Stainless steels are also successfully used in many applications such as architecture, aircraft and aerospace, electronics, food and beverage industries, home appliances, medicine, solar heating and transportation. Of recent interest, is the use of metals in the medical field [5]. For instance, stainless steels have replaced the vanadium steel plates and screws used in orthopedic surgery. By 1946, the American College of Surgeons endorsed Types 316 and 317 as the preferred grades of stainless steels and currently the low-carbon grades are employed.
Figure 1. Compositional and property linkages in the stainless steel family of alloys
2. The electrochemistry of corrosion

As in the case of a battery, the metallic corrosion proceeds by an anodic reaction, a cathodic reaction, electrolytic ion migration and current flow. The anodic reaction, the oxidation of the metal atoms, is for example the formation of ferrous ions from the steel surface:

$$\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2e$$

(1)

The possible and simultaneous cathodic reactions, depending on pH, could be one of the followings:

$$2\text{H}^- + 2e \rightarrow \text{H}_2$$

(2)

$$2\text{H}^- + \frac{1}{2}\text{O}_2 + 2e \rightarrow \text{H}_2\text{O} \quad \text{(in acid solutions)}$$

(3)

$$\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2e \rightarrow 2\text{OH}^- \quad \text{(in basic or neutral solutions)}$$

(4)

The theoretical basis for electrochemical corrosion testing is derived from the mixed potential theory [6]. The corrosion current density, $i_{corr}$, cannot be measured directly, since the current involved is one that flows between numerous microscopic anodic and cathodic sites on the surface of the corroding metal. The value of $i_{corr}$ can also be measured by another technique, generally known as “linear polarization.” This technique is based on the theoretical and practical demonstration that at potentials very close to $E_{corr}, \pm 10 \text{ mV}$, the slope of the potential/applied current curve is approximately linear [7]. This slope, $\Delta E/\Delta i$, has the units of
resistance. It has been also shown that the inverse of this slope \( \frac{\Delta E}{\Delta i} \), is related to \( i_{corr} \) according to the equation [8, 9]:

\[
i_{corr} = \left[ \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \right] \frac{\Delta i}{\Delta E}
\]

(1)

Where \( \beta_a \) and \( \beta_c \) are the anodic and cathodic Tafel slopes, respectively. It is generally accepted that the quantity \( \beta_a \beta_c/2.3 (\beta_a + \beta_c) \) is a constant \( C \). Therefore, the expression is reduced to the following:

\[
i_{corr} = C \left( \frac{\Delta i}{\Delta E} \right)
\]

(2)

On the other hand, the corrosion rate of “reactive” metals can be suppressed to a great extent by a modification of the metal surface by organic molecules or polymers. A well-known example is the corrosion protection by lacquers and other organic coatings [10-12]. This approach was used practically to protect, for example, cars against atmospheric corrosion, pipelines against corrosion in humid soil, and ships against corrosion in seawater. It was shown that the corrosion protection is due to the barrier properties of the coating, which prevents the penetration of water and oxygen to the metal/polymer interface [13]. However, many coatings are highly permeable for water and oxygen. Thus, it has been shown by Feser and Stratmann that the corrosion stability caused by coatings which are highly permeable for water and oxygen is due to specific electrochemical properties of the metal/polymer interface.
It was suggested that an important example of such electrochemical properties is the extended diffuse double layer. In the presence of defects, such as pores, which may penetrate through the coating, the diffusion barrier is lowered, and the delamination rate of the polymer defect is determined by the formation of galvanic elements. The local anode of this element being the defect and, the local cathode is, in this case the metal/polymer interface at which predominantly oxygen is reduced [16,17]. The stability of the metal/polymer interface is determined by inhibition of the oxygen reduction at the interface. It was shown that the products of the electrochemical reduction of oxygen, namely ‘OH and OH’, have detrimental effects on the chemical bonding within the polymer film [18]. From the previous discussion we can conclude that the corrosion inhibition of the coating depends to a greater extent on the composition, structure, and chemical bonding at the substrate/polymer interface than on the thickness of the coating. Thus, more attention should be directed towards improving the chemical interaction between the first monolayer of the coating and the substrate in order to improve the metal resistance to the attack of water and other aggressive ions. In this respect, the development of “molecular adhesion promoters” was suggested [19]. The molecular adhesion promoters provide a link between the substrate and the organic coating. In this respect, reactive centers are prepared on top of the substrate, which can
serve as anchor sites for suitable functional groups of the organic molecules [20, 21]. Organic compounds were successfully used as corrosion inhibitors [22]. Organic inhibitors are well known to affect the rate of metallic corrosion by decreasing the rate of either or both the anodic metal dissolution and the cathodic oxygen reduction [23].

3. **Mechanisms of Corrosion Inhibition by Organic Compounds:**

   The inhibition mechanism is generally affected by the chemical changes occurring to the inhibitor and changes to the electrolytic medium. The general possible scenarios are the partial or full dissolution of the inhibitor or its adsorption at the metal surface.

   The use of inhibitors to protect metals against corrosion is based on the ability of certain individual chemical compounds, or mixtures of these, to reduce the rate of corrosion process, or to completely suppress this process, when they introduce in small concentrations into corrosive medium. Inhibitors can vary the rate of a corrosion process only if they influence the kinetic of electrochemical reactions responsible for this process. Taking this into account, inhibitors can be classified into anodic, cathodic and mixed in view of the fact that the first type predominantly retards the anodic reaction, the second retards the cathodic reaction, while the third retards both reactions simultaneously.
Organic inhibitors, used mainly in acid electrolytes, in which the stability of the phase layer is lower, operate according to a different mechanism. In this case adsorption, and the effect which it has on the kinetic of the cathodic, are of great importance. In acid electrolytes the rate of dissolution can be reduced considerably by lowering the rate of cathodic reaction of hydrogen-ion discharge or discharge of some other depolarizing agent. Another way to reduce the dissolution rate is to remove the intermediate product of the reduction reaction from the reaction sphere. However, some effect of the inhibitors on the the anodic reaction is often observed as well [24].

For example, hydrazinium reduces the oxygen activity and adsorb at the metal/electrolyte interface. The adsorption of hydrazinium at the metal/electrolyte interface leads to the enhancement of passive film formation as in the case of benzotriazol adsorption at the copper surface [25] and benzoates on iron surfaces. On the other hand, monomolecular adsorption layers of inhibitors, known as interfacial inhibitors [26], prevent the dissolution of the substrate and the reduction of oxygen by changing the potential drop across the interface and/or the reaction mechanism thereafter. In this later case, the electric field at the outer Helmholtz plane of the double layer allows for the interaction between organic ions or dipoles and the electrified metal surface. The nature of this interaction is mainly electrostatic, during which a competitive
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adsorption between water dipoles and the organic molecule take place.

Bockris and Swinkels [27] showed that when the potential of the electrode is shifted from the potential of zero charge (PZC), at which the surface is highly charged, water adsorption is more prevailing. The organic molecule adsorption at the metal substrate, on the other hand, prevail at the vicinity of the PZC while cations and anions adsorption take place at potentials negative to PZC and positive to PZC, respectively. Specific adsorption can not exclusively be considered because of the adsorption dependence on the charge at the metal surface. It was suggested in the literature [28, 29], that the adsorption valency, the number of electrons exchanged per adsorbed molecule, is typically less than 1. The adsorption which is accompanied by a low activation energy is fast and reversible, and thus called “physisorption.” Strong interactions between the electrolytic molecules and the surface are observed in the case of “chemisorption” which is irreversible in nature [30]. The process of chemisorption is specific for certain metals, during which an electron transfer between the substrate and the adsorbed molecule may occur. Thus, the empty electronic bands of the solid substrates overlap with pair of electrons of the adsorbed molecules such as N, S, and P. This explains the slower nature of the “chemisorption” and justifies its need for a high activation energy. The electron transfer process between the molecule and the substrate is characteristic for transition metals having vacant low-
energy d-electron orbitals. On the other hand, the higher the polarizability of the heteroatom under consideration (which should possess free electron pairs) the stronger is the adsorption. Based on the Lewis acid-base concept, the inhibitor is considered the electron donor and the metal is the electron acceptor. This rationalization is in good agreement with the principle of soft and hard acids and bases (SHAB).

At this stage, it is important to distinguish between the interaction of corrosion inhibitors and molecular adhesion promoters. In the case of corrosion inhibitors, the composition and structure of the metal surface are defined by the corrosive medium. On the other hand, the surface properties can be changed and adjusted to the structure of the adhesion promoter. Moreover, while inhibitors must be soluble in the electrolytic medium and applied only for well-defined reaction conditions, adhesion promoters, however, may be applied from aqueous, nonaqueous solvents, or the gas phase and the reaction conditions can be optimized for the given substrate.

Adsorption inhibitors may be anions, cations, or neutral molecules e.g. organic molecules having an electric dipole. The protection action of adsorption inhibitors is due to a blanking effect over the entire surface.

It is very important to consider the relation between the structure of organic inhibitors, their chemical stability, and their inhibiting properties. Dealing with this relation, it was realized that the chemical
change in the nature of the organic inhibitors may occur as a result of interaction with cathodic hydrogen, corrosive medium, or dissolved metal ions. These interactions may lead to protonation, reduction, hydrolysis, decomposition, or even polymerization of the organic inhibitor. This, in turn, may lead to decrease or increase in the corrosion rate which is caused by the transformation products.

The inhibition mechanism is generally affected by thermochemical changes occurring to the inhibitor and changes to the electrolytic medium. The general possible scenarios are the partial or full dissolution of the inhibitor or its adsorption at the metal surface.

3. Corrosion inhibition of stainless steel - Methodologies and Techniques

The protection of iron and steel can be achieved in several approaches. Thus, the *cathodic protection*, in which the electrode potential is depressed to the region of immunity. This is carried out by carefully employing a reducing action on the metal surface. The sacrificial anodes of zinc or magnesium are extensively used in this context. The protection of iron and steel by *passivation or oxidizing inhibitors* is another alternative. In this later case, the electrode potential of the metal can be raised to the region of passivity by adding oxidizing inhibitors (such as chromates), by anodic polarization of the metal substrate in a given electrolyte, or by alkalization of the solution.
other major means of protection of iron and steel against corrosion are the adsorption of inhibitors to the metal surface (as discussed in the previous section), the use of impermeable coatings (such as paints, metallic coatings, plastic coatings, etc.) and rubber.

In the following section, the candidate will survey some of the recent literature concerning the methodologies and techniques for the corrosion inhibition of steels. Fujimoto et al. showed recently that the pitting corrosion resistance of type 304 stainless steel can be improved by modification of the steel passive film with ultraviolet light irradiation [31]. They showed that the pitting potential shifts to the positive direction by exposing the surface of the steel to UV light during the passivation step. Moreover, the pit generation rate, was lowered by half an order of magnitude following UV light exposure during passivation, while the repassivation rate, was unaffected. X-ray photo-electron spectroscopy revealed additional chromium enrichment in the passive film after exposure to UV light during passivation, and this is thought to be related to the suppression of the pit generation rate. Specific types of corrosion can be also inhibited using specific cations or anions. Thus, Aballe et al. [32] mentioned that lanthanum, cerium and samarium chlorides can be used as uniform and pitting corrosion inhibitors of AISI 434 and AISI 304 stainless steels in 3.5% NaCl aerated aqueous solutions. The inhibition efficiency was evaluated by using
Electrochemical techniques such as linear and cyclic polarization which was cathodic in nature and confirmed by SEM and energy dispersive spectroscopic techniques. In a similar study, the influence of sulfate ions on the stress corrosion cracking for stainless steel AISI 321 with constant strain rate in aqueous chloride solution at relatively high temperatures was examined [33]. In this work the steel specimens were tested in solutions with $10^{-2}$ M Na$_2$SO$_4$ and $10^{-3}$ M NaCl and $5 \times 10^{-3}$ M NaCl at 150 and 280 °C. The presence of SO$_4^{2-}$ in Cl$^-$ solutions increases the time to fracture and the reduction of area in comparison to pure Cl$^-$ solution. The authors explained their observation in terms of the lower concentration of corrosive hydrogen near the fracture surface in comparison with tests in Cl$^-$ solutions.

Corrosion inhibition of mild steel in acid solution by alkylamines (ALK-AM) and aniline hydrochloric (ANL-HCl) salts was investigated in the presence of sodium sulfate and sodium chloride using a potentiostatic, scanning electron microscope and fourier transform infrared techniques [34]. Results showed chloride ions have a pronounced effect on inhibition of amines and ANL-HCl for corrosion of mild steel. In the presence of Cl$^-$ ions, cationic type surfactants were attached to the surface through formation of chloride precipitate at the surface. In the absence of the organic inhibitor, corrosion initiated along the grain boundaries of ferrite and pearlite structures. In the presence of organic inhibitor,
however, the steel surface was covered by an organic salt precipitation and corrosion was reduced. In another study, sulphamethoxazole was tested as corrosion inhibitor for mild steel in HCl solution using potentiodynamic polarization and weight loss techniques [35]. Results showed that the sulphamethoxazole is an effective inhibitor for mild steel in this medium. The inhibition was assumed to occur via adsorption of the inhibitor molecule on the metal surface. The protection efficiency increases with increasing inhibitor concentration but decreases with increasing temperature. On the other hand, the effect of changing functional groups of some amides and thiosemicarbazone derivatives on their inhibition efficiency has been studied on mild steel [36]. Results showed the mechanism of corrosion inhibition and considered the total molecular structure of the inhibitor that relates to the nature and spatial relationship of the different functional group. All the compounds studied inhibited the corrosion to varying degrees. However, molecules that possessed a thiocarbonyl group, such as thiourea, thioacetamide, and thiosemicarbazide have higher inhibition efficiency than the corresponding compounds that do not, such as urea, acetamide and semicarbazide. In another study, the effect of a 2,5-disubstituted 1,3,4-oxadizoles, on corrosion of mild steel in 1 M HCl and 0.5 M H₂SO₄ have been investigated [37]. The results revealed that these compounds are very good inhibitors and behave better in 1 M HCl than 0.5 M H₂SO₄.
These compounds acted on the cathodic reaction without changing the mechanism of the hydrogen evolution reaction. The changes in impedance parameters, namely the charge transfer resistance \( (R_t) \) and the double layer capacitance \( (C_{dl}) \) indicated the adsorption of the inhibitor at the surface of the steel. It was shown that the adsorption mechanism of these derivatives in acidic media followed a Langmuir adsorption isotherm. In another publication [38], the objective was to evaluate the effect of changing functional and structural groups on the protection efficiency imparted by various inhibitor molecules. It was found that the molecules that possessed a thiocarbonyl group exhibited much higher protection efficiencies than corresponding compounds that did not. Furthermore, it made only little difference whether the thiocarbonyl group was attached to two amino or methyl groups. However, above certain concentrations they lose their efficiency and eventually become corrosion promoters. These results are in good agreement with those obtained recently by Lagrene et al.

Thiourea and derivatives have been studied as inhibitors for mild steel [39]. Results showed that the inhibitor efficiency increased with molecular weight and inhibitor concentration. Higher inhibitor concentrations decreased hydrogen pickup. Thiourea accelerated corrosion reaction and hydrogen pickup at higher concentrations. Potential studies showed that cathodic reaction was inhibited at lower
concentrations of inhibitor. Moreover, anodic reactions were inhibited at higher concentrations and results were based on the Langmuir adsorption isotherm. In other study, the inhibiting action of linear and cyclic thiocarbamides on mild steel corrosion in 1 M HCl was examined [40]. It was found that the inhibiting effect of these compounds increased with the temperature of the corrosion medium. The presence of inhibitor in the solution decreases the apparent activation energy of the hydrogen evolution reaction. Inhibitor chemisorption on the metal surface was described by the Temkin adsorption isotherm. The thiocarbamides studied are adsorbed through the sulfur atom that is the adsorption center, forming a donor-acceptor between the unpaired electrons of the sulfur atom and the positive center of the metal surface. Ita and Offiong [41] indicated from weight loss and hydrogen evolution measurements that 4-phenylsemicarbazide and semicarbazide actually have very significant effect on corrosion of mild steel in HCl acid. Generally, the inhibition was found to increase with increase in inhibitor concentration and in half-life, but with a decrease in temperature and decrease in the first-order rate constants obtained at 30 °C and 40 °C. The results showed that a physisorption mechanism was obeyed and the inhibitors followed the Freundlich adsorption isotherm.

The influence of the organic sulfur-containing compounds on the corrosion of ferritic and austenitic stainless steel in sulfuric acid was
studied [42]. The results showed that the anodic dissolution and self-corrosion of stainless steel were remarkably accelerated in solution in presence of a low amount of the organic sulfur-containing compounds, ca. 0.02 mmol.dm$^{-3}$. With an increase of the inhibitor concentration the molecules adsorbed on the surface and segregated the metal surface from the solution, that decreases the anodic dissolution and hydrogen evolution current of the stainless steel. On the other hand, 2-aminobenzothiazole and its derivatives were synthesized, and their inhibitive-action on the corrosion of mild steel in 1 M HCl acid was investigated [43]. All these compounds were found to reduce the permeation of hydrogen through mild steel in HCl solution. The determination of the inhibition efficiency of these compounds at different temperatures indicated that 2-amino-6-chlorobenzothiazole showed the best performance over 2-aminobenzothiazole, 2-amino-6-methyl benzothiazole, and 2-amino-6-methoxy benzothiazole. Moreover, the study showed that this class of inhibitors acted as a cathodic type, and the adsorption of these compounds obeys Temkin adsorption isotherm. The inhibitive action of thiourea and its derivatives was investigated on corrosion of AISI 410 stainless steel using weight loss measurements, potentiodynamic polarization and scanning electron microscopy technique [44]. Results showed that they are effective inhibitors and they obey Langmuir adsorption isotherm. In this investigation, thiourea, alkylthiourea, and n-
n-phenylthiourea were studied, with n-phenylthiourea showing the highest surface coverage and hence being the most efficient inhibitor.

The effect of chloride concentration on early stages of pitting for Type 304 stainless steel has been studied using an AC impedance method. The Warburg impedance coefficient, which is calculated from Bode plots, increases with increasing chloride concentration at low potentials in the passive region when the diffusion process begins to occur at the surface. In their study, Hong and Magumo [45] found that for a pit which is nucleated under a given potential, there exists a minimum chloride concentration above which the pit on the surface of the steel can be activated into metastable propagation, and below which it cannot. Moreover, it was found that the value of pitting potential increases linearly with the logarithm of chloride concentration of solution. The influence of propargyl alcohol and some ethoxylated fatty acids on the corrosion behavior of mild steel in H₃PO₄ and sulfuric acid were investigated over a range of acid concentrations and solution temperature by using electrochemical measurements [46]. Propargyl alcohol was found to inhibit the cathodic reaction at temperatures ≥ 40 °C by adsorption at the steel surface. It was also found that the adsorption is most favorable at a surface partially covered by adsorbed hydrogen. For the uninhibited H₃PO₄ solutions, a straight-line relationship was found between the corrosion rate and the logarithm of acid concentration. On
The other hand, the inhibition efficiency increases with increasing the concentration and chain length of the fatty acids for mild steel in 1.0 M sulfuric acid and decreased by temperature [47]. In another study by Lemaitre, the presence of halide ions in an electrolyte can provoke local breakdown of the passive film of stainless steel in initiate the localized corrosion by different exposed mechanisms, resulting in stress corrosion cracking crevice corrosion or pitting. The efficiency of the presence of other oxyanions with chloride to prevent the risk of pitting corrosion is shown by the use of polarization curves or impedance measurements and calculated by the statistical studies of the pitting potential values [48].

The chemical etching, the determination of pitting potential and I-t curves, the test of simulated occluded cell and electrochemical impedance spectra were used in this work. Both sodium dodecyl benzene sulfonate and monoethanolamine were proved to act as inhibitors for stainless steel in solution of chloride to prevent pitting corrosion during the periods of initiation and propagation, and that the mixture shows synergetic inhibition, especially during the propagation of the pitting [49]. The pit generation rate was measured on Type AISI stainless steel 304 in chloride and chromate containing media by a statistical method [50]. Inhibition efficiency was calculated, and an inhibition diagram was constructed from the parameters obtained, showing a competitive phenomenon between the two species in solution. An experimental equation for the
between the two species in solution. An experimental equation for the decrease of the pit generation rate was obtained in the pitting domain of the diagram, indicating that adsorption was the limiting stage of the inhibition mechanism. It was suggested that the ion playing the role of the inhibitor species was not \( \text{CrO}_4^{2-} \) but \( \text{HCr}_2\text{O}_7^- \). The presence of chromate allowed the pH value to stabilize near the active site. A diffusion process occurred with an increase of the thickness of the passive film due to inhibitor presence. When all sites were covered by the inhibiting species in the inhibition domain, adsorption was stopped and diffusion was the limiting process. A study published by Dhirendra [51], showed the effect of Cl\(^-\) content (0.007 – 0.12 g/100 ml) at 100% relative humidity in air on the corrosion of austenitic stainless steel in 24 hours was evaluated by weight loss. The corrosion increased with increasing Cl\(^-\) to 0.05g/100 ml but practically no increase in corrosion was observed at higher Cl\(^-\) content. The efficiency of protection by treatment with 1% solution of a newly developed corrosion inhibitor DX-A increased to 85%. The corrosion resistance of 13Cr stainless steel tubing in CO\(_2\) offshore wells was evaluated [52]. Based on uniform and pitting corrosion NaCl solutions in down-hole corrosion, the sensitization is prevented by stress-relief heat treatment at \(< 300 ^\circ \text{C}\) or annealing at \(> 650 ^\circ \text{C}\). In the same study, crevice corrosion of pipe-thread coupling was reduced by tight metal-to-metal seals, greased copiously and by surface
treatment by oxalate. However, galvanic corrosion of carbon steel occurs in contact with the stainless steel. The corrosion of stainless steel was limited at 30 bar CO$_2$ and 120° C and no need arose for inhibition treatment.

The electrochemical and corrosion behavior of mild steel in 1 M H$_2$SO$_4$ solution containing some selected thiols namely, 2-mercaptobenzothiazol, 2-mercaptobenzimidazol, and 2-mercaptobenzoxazol together with halide ions have been studied by galvanostatic polarization technique, at temperatures ranging from 30 to 60 °C [53]. The effect of temperature on the inhibition efficiency of both investigated thiols and halide ions was studied. The presence of halide ions together with thiols caused a shift in the corrosion potential as well as the linear part of the cathodic Tafel line to the anodic direction. The corrosion process was found to be under activation control. Moreover, the inhibitors did not change the mechanism of the corrosion process. The thermodynamic parameters for adsorption of thiols were also calculated.

Electrochemical techniques were employed to compare and contrast the roles of alloyed Mo and aqueous MoO$_4^{2-}$ in enhancing pitting resistance of ferritic stainless steel in neutral chloride solutions at 80 °C [54]. Alloyed Mo inhibits pitting in 0.14 N and 1 N chloride solutions while aqueous MoO$_4^{2-}$ inhibits in the diluted Cl$^-$ solutions only. Prepassivation experiments show that the major role of high Cl$^-$
concentrations is to prevent MoO$_4^{2-}$ from forming a passive film rather than in attacking the film after it has formed. Alloyed Mo and aqueous MoO$_4^{2-}$ inhibit through incorporation into the passive film but incorporation from the solution is easily influenced by solution variables such as chloride concentration.

6. Factors affecting the rate of corrosion and efficiency of inhibition

The influence of factors which can increase or decrease the rate of pH reduction and halide ion build up in a developing pit solution were evaluated for pits nucleated on the surface of a commercial grade 316L [55]. Temperature and applied potential were shown to have a significant influence on these processes for the steel immersed in Cl$^-$ and Br$^-$ solutions and not in F$^-$. Additions of appropriate buffers to chloride test solutions was shown to alter quite considerably the extent of pH reduction in growing pits and in a number of cases to increase the pitting potential also. Moreover, in chloride solutions containing suitable amounts of sodium dichromate the passivation behavior of 316L was shown to alter considerably with the almost total elimination of activation-repassivation events on the oxide surface as evidenced by the absence of current peaks or fluctuations on potentiostatic current time plots. On the other hand, inhibition efficiencies of different concentrations BMAT (benzoimidazole compound) on 316L ss in 5%
HCl were tested by weight loss measurements [56]. BMAT sorption obeyed the Frumkin isotherm adsorption model. The corrosion inhibition was considered to be chemisorption by studying the influence of temperature on 316L SS. Testing of polarization curve showed that BMAT was mainly cathodic inhibitor.

The effects of alloying elements on the localized corrosion resistance of austenitic SS are considered in terms of anodic and cathodic reaction inhibition [57]. Surface analysis has confirmed that when local attack takes place nitrogen enhances the anodic segregation of beneficial alloying elements, such as Cr and significantly prevents the transpassive dissolution of Mo. Alloyed chromium, molybdenum and nitrogen, all improve the localized corrosion resistance of stainless steel by inhibiting the anodic process. However, in order to further increase localized corrosion resistance, it was also necessary to constrain the cathodic reaction. It was shown that cerium ion implantation of UNSS 31603 stainless steel was very effective in inhibiting the cathodic electrode reaction involved in metallic corrosion. As a result of the inhibition of the kinetics of electrode processes, cerium treatment improved the localized corrosion resistance, and especially crevice corrosion resistance. This was supported by the results of electrochemical measurements in aerated 0.6 M NaCl + 0.1 M Na₂SO₄, and by accelerated corrosion tests.
Pitting corrosion behavior of commercial stainless steels type 904L and 316L was investigated in pure sodium chloride solutions of different pH values and at different temperature [58]. In this study, potentiodynamic polarization technique and SEM were utilized. Pitting corrosion of 316L stainless steel occurred readily at 30 °C and in all chloride solutions of concentrations ranging between 10-3 mol/m³ while 904L stainless steel did not pit at temperatures lower than 40°C and 0.6 mol/m³ NaCl, respectively. Pitting potential for 904L stainless steel was much more noble than that obtained for 316L stainless steel while the protection potential values were almost the same for both alloys. The pitting corrosion inhibition by OH⁻ ions was more pronounced for 316L SS and E(pit) approached that obtained for 904L SS in alkaline solutions. The alloy with higher Cr, Ni and Mo content 904L SS was more sensitive to the temperature effect as compared to 316L. E(pit) was dependent on the alloy composition while the protection potential, E(prot), was not affected by the alloy composition. Another study describes the temperature dependent pitting potential behavior of austenitic stainless steel in neutral chloride solutions between 10 and 70 °C [59]. Two chloride ion concentrations 0.1 and 0.5 M were chosen in this study. Molybdate ion additions were between 0.01 and 0.1M. While the pitting potential of AISI 304 stainless steel decreased continuously with temperature, AISI 316 stainless steel had a temperature independent
region after 50 °C. When molybdate ions were added into the solution, the pitting potential of AISI 304 SS also became temperature independent after 50 °C. The pitting potential change the by the addition of molybdate ions, defined as inhibition efficiency, increased with increased molybdate/chloride ratio and temperature. The pitting inhibition efficiency obtained by the addition of sulfate ions decreased with the increase of temperature. The addition of molybdate ions after initiation of pitting in AISI 304 SS, repassivated the pits and shifted the pitting potential. The pronounced beneficial effects of molybdate ions on the propagation of pitting, was attributed to the conditions favoring the reduction and precipitation of the reduction products of molybdate ions.

Another comparison was mentioned, that is the effect of dissolved oxygen on the corrosion of carbon steel and stainless steel SUS 304 and 316L in pure water containing < 5-1000 ppb dissolved oxygen by a recirculating plant simulating BWR conditions at 288 °C for 1000 hours [60]. The corrosion weight loss and metal release amount decreased in the order of carbon steel > SUS 304 > SUS 316L. The corrosion of carbon steel decreased with increasing dissolved oxygen concentration. At < 5 ppb dissolved oxygen, the corrosion of SUS 304 was inhibited by a Cr-rich film and that of SUS 316L by an oxide film containing Mo, Ni, and Cr. The corrosion resistance of SUS 304 and 316L increased by Fe and Ni ferrite films at >100 ppb dissolved oxygen. The metal distribution
in the oxide films varied with immersion time and dissolved oxygen concentration.

The anodic behavior of high purity stainless steels based on 316L-composition, was studied at room temperature in HCl solutions from 1 to 6 M [61]. For all acid concentrations, the presence of 0.22% N had little or no effect on the active dissolution kinetics at low overpotentials. The effect on the critical current density for passivation was small for low HCl concentrations (< 3 M). At high HCl concentration (> 4.5 M), no passivation occurred and again N had a little effect. For HCl concentration approximately 4 M, N reversibly impedes active dissolution at a few hundreds mA/cm². The effect did not appear to be an oxide passivation, but was more likely due to surface enrichment of N atoms. Implications for localized localized corrosion were discussed. Moreover, an effect similar to that of N alloying is reproduced on a N free alloy by adding 2 M NaNO₃ to a 4 M HCl solution. This effect was distinct from the passivation of salt-covered surfaces and may be preferable to the later as an explanation of the increase in pitting potential by NO₃⁻ addition to NaCl solutions. Passivation under a salt film was suggested to explain the passivation of growing pits above the inhibitions potential. In another study, The kinetic of the electrochemical reactions occurring during the initiation and propagation of crevice corrosion were investigated using electrochemical impedance measurement [62]. Two
types of crevice formed were used and comparable results were obtained. The initial stage of crevice corrosion is similar to that previously observed for the initiation of pitting corrosion of 316L SS but at lower potentials. The crevice would appear to encourage the build up of a local environment suitable for the acceleration of the metal dissolution or inhibition of the film repassivation processes. A stochastic process of film rupture and chloride adsorption was proposed based on the observed changes of capacitance, potential and charge transfer. The initial corrosion follows a rate law that reached a maximum some 10-20 h after immersion and then decreased to a relatively steady value. Higher frequency capacitance values indicated a change from passive film condition to active electrochemical dissolution whereas the lower frequency response indicated the increasing role of an adsorption during initiation that then changed to diffusion as the crevice corrosion propagated. Habeeb et al. [63] explained the inhibition efficiency of two mixtures of organic substances, ca. quinoline + thiourea and quinoline + methyl methacrylate (stabilized with 5% hydroquinone) using a potentiodynamic polarization technique. Tests were made on stainless steel 316L and 316MA in 5% H₂SO₄ at 25-65 °C. The inhibition efficiency was calculated from the corrosion current density. The mixture of 0.05 N quinoline with 0.05 N methylmethacrylate gave good protection of the steels, and the inhibition efficiency was better at 25 than
Different types of organic substances, namely an acetylenic derivative, and sulfur or nitrogen-containing additives, were tested as inhibitors for intergranular corrosion of sensitized AISI 304 stainless steel, in diluted sulfuric or sulfamic acid solutions at 70 °C [64]. Among the different organic substances examined, the sole compounds able to stop the intergranular attack are those containing sulfur atom with its electronic lone pair free. These inhibitors accomplish their action by reducing the differences of the corrosion rate between the chromium-depleted grain-boundaries and the matrix. As some of the tested inhibitors could decompose with the formation of HS⁻ or H₂S, the influence exerted by HS⁻ ion on the corrosion process is evaluated.

Corrosion of iron in 2 M HNO₃ has been studied by the electrochemical polarization and weight-loss measurements [65]. The effect of some thiophene derivatives has been investigated. The results showed that the inhibitors influence both the cathodic and anodic processes, and are adsorbed on the metal surface in molecular form. They do not change the mechanism of reaction between the iron and nitric acid but decrease its rate. This effect is controlled by the values of their dipole moments. In another study, the adsorption from solution of chloroacetic acid at low carbon steel surface has been measured using
Langmuir and Bockris-Swinkels isotherm [66]. The coverage has been determined and the standard free energy of adsorption was about 4 KJ/mol. The adsorption arises largely from metal-adsorbate dispersion interface differences between water and organic acid. A knowledge of the adsorption of organic acids at the electrode–solution interface is needed for understanding of organic electrode reactions and the inhibitive action of organic acid on corrosion.

The corrosion inhibition effect of glycol-ether-diamine-tetra-acetic acid on stainless steel SUS 304 was electrochemically examined in deaerated 2% NaCl solution at 30 °C [67]. Glycol-ether-diamine-tetra-acetic acid was chemically adsorbed on the steel surface and the film had a good thickness, strong binding energy, and uniformity. The film had high corrosion inhibition effect at pH 2-9 and high concentration of Cl but was unsuitable against oxidizing agents. The anticorrosive efficiency was 16.01% in 6 % FeCl₃ solution at 35°C. In another study, a series of compounds having N-acylamino acid or related structure were investigated as potential inhibitors or localized corrosion of AISI 304L stainless steel [68]. The effect of these compounds on the breakdown potential was measured using the linear current scan method. Interaction of the inhibitors with electrode surface was studied using capacitance measurements and correlated with solution surface tension measurements. Successful inhibitors interact strongly with the AISI 304L surface, but the
inhibition effect appears to involve more than just adsorption of a hemimicellar inhibitor layer, which could exclude Cl\(^{-}\) from the surface or provide surface pH buffering. Formation of such a layer is sensitive to the structure of the compound. Trabanelli et al. tested different types of organic containing additives (N-containing, S-containing, and acetylenic derivatives) as inhibitors for the intergranular corrosion of a sensitized AISI 304 stainless steel in 1 N sulfamic acid solution at 70 °C [69]. Only S-containing additives inhibit intergranular in sulfamic acid solution. Among the organic additives tested (without sulfur) only benzotriazole and the N-containing inhibitor decrease the severity of the localized attack in hot, diluted sulfamic acid solutions. In the presence of the S-containing additives, the corrosion rate of sensitized SS specimen is equal to that of a non-sensitized specimen.

A slow strain rate \((10^{-6} \text{ s}^{-1})\) was used to study the possibility of inhibiting or delaying the stress corrosion cracking (SCC) of AISI 304 stainless steel wires in 1 M HCl solutions at room temperature by using organic additives [70]. Some of the tested organic substances (phenylthiourea, benzimidazole-2-thiol, and benzothiazole-2-thiol) inhibit SCC in the quoted environment. The results obtained in tests of long duration on U-bent specimens. The efficient SCC inhibitors manifest their action on either the incubation stage or the propagation stage of the
SCC process. The action of the inhibitors cannot be directly correlated with the corrosion potential of stainless steel wires tested.

7. High-Grade steels

A review on the corrosion mechanism of high-Cr stainless steel was presented in the literature [71]. Good adhesive, corrosion-inhibiting-Cr$_2$O$_3$ coatings (some nm-thick), were formed on the steel surface. A local depletion of Cr ($< 10\%$) leads to a loss of the corrosion inhibiting layer, and therefore to an accelerated metal dissolution. Simultaneously, the carbide (Cr, Fe) 23C6 is formed at the grain boundaries. Intergranular corrosion starts at the Cr-depleted grain boundaries. In another study, weight loss measurements were performed in 20\% and 28\% HCl at 90 °C on C steel X65, 22Cr5Ni duplex stainless steel, and 2 superaustenitic steels in presence of organic substance [72]. The organic substances tested were quaternary ammonium salts. The synergistic effect of KI on the inhibitive efficiency of the organic substance was studied. The variation of corrosion rate during the test time, normally 6 hours were recorded. The corrosion rates of the four steels examined were reduced to $< 1 \text{mg/cm}^2$ using ternary inhibitor mixtures containing quaternary ammonia salts, trans-cinnamaldehyde and 0.2\% of each component. On the other hand, corrosion of stainless steel reactors in the manufacture of nitrogen containing organic phosphonic acids, was prevented by contracting the reactor with HNOx (x= undefined), to form a layer of
$\text{MNO}_3\ (M=\text{metal})$, such that the reactor product stream contains corrosion products content of Ni 10.1-2, Mo 0-0.3, and Fe 0.2-3 ppm [73]. Thus, a stainless steel reactor was treated with 98% HNO$_3$, then a mixture of ammonium sulfate, 37% HCHO, and phosphorous acid passed through the reactor at 105 °C producing 97% conversion to N-[CH$_2$PO(OH)$_2$)$_3$, with the product stream containing Ni 0.5, Mo and F 2 ppm, vs. 90.5, 70, 20 and 300, respectively for a stainless steel reactor not treated with HNO$_3$. 
AIM OF THE THESIS
The corrosion of stainless steels in acidic and in aggressive media such as those containing-chloride is of great importance to the industrial processes. The goals of the present thesis is to investigate the effect of using a new class of organic inhibitors on the corrosion behavior of stainless steel type 316 in sulfuric acid. The candidate will attempt to clarify important issues, among them:

- To study the electrochemical behavior of stainless steel type 316 in sulfuric acid medium.
- To study and compare the electrochemical characteristics of the stainless steel in sulfuric acid solution of different concentrations.
- To apply and compare the effect of some thiophene derivatives on the corrosion behavior of stainless steel in acidic and in chloride-containing acidic media.
- To correlate the geometrical factor imparted by the different inhibitors on the experimental results obtained.
- To investigate the effect of temperature on the adsorption characteristics of the inhibitors at the stainless steel surface.
- To estimate the thermodynamic parameters of the adsorbed organic layers of the inhibitor at the stainless steel surface, such as $\Delta H^\circ$, $\Delta S^\circ$, $\Delta G^\circ$ for the adsorption process.
EXPERIMENTAL WORK
1. Materials and reagents

1.1 stainless steel sample

AISI 316 stainless steel was used in this study, with the percentage chemical composition listed in Table 1. The stainless steel sample was purchased from Goodfellow (Huntingdon, England).

Table 1: Percent chemical composition of stainless steel 316 used in this study.

<table>
<thead>
<tr>
<th>Element</th>
<th>% composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>16.9</td>
</tr>
<tr>
<td>Ni</td>
<td>10.9</td>
</tr>
<tr>
<td>Si</td>
<td>0.75</td>
</tr>
<tr>
<td>Mn</td>
<td>1.24</td>
</tr>
<tr>
<td>N</td>
<td>0.025</td>
</tr>
<tr>
<td>S</td>
<td>0.027</td>
</tr>
<tr>
<td>Cu</td>
<td>0.20</td>
</tr>
<tr>
<td>Mo</td>
<td>2.11</td>
</tr>
<tr>
<td>C</td>
<td>0.053</td>
</tr>
<tr>
<td>Fe</td>
<td>Balance</td>
</tr>
</tbody>
</table>

1.2 reagents and solutions preparation

Sulfuric acid, Sodium chloride, 2-Thiophene carboxylic hydrazide (TCH), 2-Thiophene carboxylic acid (TCA), 3-Thiophene carboxaldehyde (TCAL), 2-Acetyl thiophe ne (AcT). The structure and some properties of the inhibitors used in this study are shown in figure 1. All chemicals purchased were used as received and
Figure 1. List of Compounds Used as Inhibitors in the Present Study
were supplied by Aldrich Chem. Co (Wisconsin, USA). Test solution were prepared from stock and diluted using de-ionized water supply. Water was first distilled and then de-ionized using Millipore water purification system. The conductivity of water used in this study is 18.3 μS.

1.3 Electrode Mounting and Electrochemical Cells

AISI 316 stainless steel specimens were in the form of rods and sheets. Rod specimens were prepared and mounted according to the following steps: stainless steel rods were cut in the dimensions of 2.0 cm long and 0.60 cm diameter. The stainless steel specimen was then grooved and threaded for electrical contact and connection. A copper rod 12.0 cm long and 0.35 cm diameter was used for establishing electrical contact. The whole assembly was finally intersted in a glass tube 10.0 cm long and 0.8 cm inner diameter. Epoxy resin (Torr Seal, from Varian, MI, USA) was used to ensure the exposure of a determined apparent surface area of 0.283 cm². This specimen configuration was used for electrochemical measurements.

Flat specimen configuration was used for samples prepared for surface examination. In this setup, the stainless steel foils in the dimensions of 5 cm x 5 cm and 2 mm thick were cut and
mounted on a flat cell holder. The surface area exposed is either 1.0 cm$^2$ or 5.0 cm$^2$ according to the cell used.

Prior to each electrochemical measurement, the steel specimen subjected to surface experiments was prepared according to the following steps: the surface was polished mechanically using metallurgical papers of successive grades (120-600-1200 μm). The surface was then polished using alumina paste 0.3 μm dispersed on a soft cloth paper until a scratch-free surface is obtained. The surface was rinsed with distilled water, degreased in ethanol and was thoroughly rinsed with de-ionized water.

Two types of electrochemical cells were used in this investigation. A three-electrode one-compartment glass cell, with a saturated Ag/AgCl reference electrode and a platinum sheet (2 x 2 cm$^2$) counter electrode was used for the electrochemical measurements.

The second type of cells, is a one-compartment three electrode flat cell that was used to prepare the surface specimens.

Figure 2 shows diagram of the electrochemical cells used.
Conventional one Compartment Cell

Figure 2.b Flat Cell
2. Equipments and instrumentation

2.1 Electrochemical equipment

All the different electrochemical measurements, potentiodynamic, tafel and polarization resistance measurements were carried out with the Gamry PC3/750 mA potentiostatic / Galvanostal /ZRA system (Gamry, Inc., USA), and electrochemical analysis was performed using the Gamry framework software.

2.2 Surface Instrumentation

The specimen surface with inhibitor formed layer was characterized using scanning electron microscopy SEM equipped with an energy dispersive x-ray analyzer EDXA, surface reflectance fourier transform infra-red spectroscopy SRFT-IR, x-ray diffractin XRD, and x-ray photoelectron spectroscopy XPS. A Jeol Model JSM-5600 SEM equipped with EDXA capability was used for surface morphological determination. The instrument is fully computerized with 18-300,000 times magnification power, with guaranteed resolution of 3.5 nm, acquisition of both secondary and back-scattered electron images. The samples were coated with a thin film of gold to eliminate the effect of charging during measurements. A Jeol JFC-1200 fine coater was used for this
purpose and a current of 20 mA was applied for 150 s coating period.

3. **Solutions preparation and solvents.**

All solutions were prepared from reagent grade chemicals and de-ionized water. The 0.5 M H$_2$SO$_4$ was prepared by dilution from the stock concentrated sulfuric acid (5 M).

Different concentration of the inhibitors were prepared by dilution of the stock of 0.1 M of the inhibitor (table 2. shows the needed solvent to prepare the stock solution), and then diluted by de-ionized water to the different concentrations of 5x10$^{-4}$ M, 1x10$^{-3}$ M, 5x10$^{-3}$ M, and 1x10$^{-2}$ M.

Table 2. A list of the inhibitors and suitable solvents for each inhibitor.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Solvent and Dilution Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCH</td>
<td>0.5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>TCA</td>
<td>7 ml ethanol and then diluted with 0.5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>TCAL</td>
<td>5 ml ethanol and then diluted with 0.5 M H$_2$SO$_4$</td>
</tr>
<tr>
<td>AcT</td>
<td>5 ml ethanol and then diluted with 0.5 M H$_2$SO$_4$</td>
</tr>
</tbody>
</table>

4. **Electrochemical Measurements**

All electrochemical measurements were performed at room temperature (ca. 25° C) except for those experiments concerning temperature coefficient. A three electrode cell was used for all measurements.
4. Electrochemical Measurements

All electrochemical measurements were performed at room temperature (ca. 25° C) except for those experiments concerning temperature coefficient. A three electrode cell was used for all measurements.

4.1 Potentiodynamic Polarization measurements

Table 3. shows the measurements conditions for the potentiodynamic measurements. The potentiodynamic polarization measurements were performed to study the complete behavior of the current in the wide potential range scan. These measurements were carried for 316 stainless steel in presence and absence of the different inhibitors.

Table 3. Potentiodynamic Polarization experimental conditions

<table>
<thead>
<tr>
<th>Initial Potential</th>
<th>-1 V vs. $E_{\text{reference}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Potential</td>
<td>1.5 V vs. $E_{\text{reference}}$</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>5 mV/s</td>
</tr>
<tr>
<td>Initial Delay</td>
<td>1200 s</td>
</tr>
</tbody>
</table>

$E_{\text{reference}}$: vs. Ag/AgCl

4.2 Polarization Resistance measurements

Table 4 lists the experimental conditions for the polarization resistance experiments.
Table 4. Polarization Resistance experimental conditions

<table>
<thead>
<tr>
<th>Initial Potential</th>
<th>-0.02 V vs. ( E_{\text{open circuit}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Potential</td>
<td>0.02 V vs. ( E_{\text{open circuit}} )</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>1 mV/s</td>
</tr>
<tr>
<td>Initial Delay</td>
<td>300 s</td>
</tr>
</tbody>
</table>

4.3 Tafel measurements:

Table 5. Tafel measurement conditions

<table>
<thead>
<tr>
<th>Initial Potential</th>
<th>-0.250 V vs. ( E_{\text{open circuit}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Potential</td>
<td>0.250 V vs. ( E_{\text{open circuit}} )</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>1 mV/s</td>
</tr>
<tr>
<td>Initial Delay</td>
<td>300 s</td>
</tr>
</tbody>
</table>

4.4 EIS measurements

The specimen was left under open circuit conditions for 300 s. At this stage the open circuit potential, \( E_{\text{open}} \) was determined. The onset potential of \(-0.1\) V and \(-0.2\) V were chosen as the DC signal of EIS experiment.

Table 6. EIS experimental conditions

<table>
<thead>
<tr>
<th>Frequency Range</th>
<th>0.02 – 5000 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC Potential</td>
<td>10 mV</td>
</tr>
<tr>
<td>DC Potential</td>
<td>-0.1 or-0.2 mV vs. ( E_{\text{open circuit}} )</td>
</tr>
<tr>
<td>Initial delay</td>
<td>300 s</td>
</tr>
<tr>
<td>Inhibitor concs.</td>
<td>0, 5\times10^{-4}, 1\times10^{-2} M</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>0.5 M ( \text{H}_2\text{SO}_4 )</td>
</tr>
</tbody>
</table>
5. Surface characterization

A flat type three-electrode electrochemical cell, with saturated Ag/AgCl reference electrode and a platinum counter electrode, was used to prepare the sample. Surface area 5.3 cm² according to the cell used. The electrochemical cell was a pyrex glass cylinder with a flat circular piece of glass fused on each end. Two small holes on the top of the cylinder connected with two plastic tubes were used to accommodate the gas bubbler. A platinum sheet counter electrode of large area was housed inside the chamber. A cavity was left at the top of the chamber to be filled with the testing solution and to insert the reference electrode. The cavity is connected to the working electrode through a Luggin capillary tube (cf. Figure b).

Then a potential static measurement was performed by applying a potential of 1.5 V for 10 minutes vs. E\text{reference}, then the sample was subject to the intended surface measurement.

<table>
<thead>
<tr>
<th>Initial Potential</th>
<th>-0.5 V vs. E\text{reference}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Time</td>
<td>60 s</td>
</tr>
<tr>
<td>Final Potential</td>
<td>1.5 V vs. E\text{reference}</td>
</tr>
<tr>
<td>Final Time</td>
<td>600 s</td>
</tr>
<tr>
<td>Limit I</td>
<td>250 A</td>
</tr>
</tbody>
</table>
1 Scanning Electron Microscope SEM

Samples of 316 stainless steel investigated by SEM were in the form of sheets with surface area of 5.3 cm². The samples were exposed to the different medium of:

a) 0.5 M H₂SO₄

b) 0.5 M H₂SO₄ + 10⁻² M TCH

c) 0.1 M H₂SO₄ + 0.01 M NaCl

d) 0.1 M H₂SO₄ + 0.01 M NaCl + 0.01 M TCH

2 Surface Reflectance FT-IR Spectroscopy

Two 316 stainless steel samples were examined by FT-IR spectroscopy.

a) Unexposed sample.

b) And sample exposed to 0.1 M H₂SO₄ + 0.01 M TCH.

In order to examine the layer of the inhibitor built on the stainless steel surface.
RESULTS AND DISCUSSION
Evaluation of some thiophene derivatives for the inhibition of stainless steel:

Thiophene compounds possess aromatic molecules in which one carbon atom is replaced by a heteroatom, sulfur. The structure of the thiophene derivatives used in the present study is shown in figure 1. Thiophene compounds are used extensively in the preparation of several organic-based drugs [74], and recently in the preparation of organic conducting polymers [75]. The nature of substituent in the ring changes considerably the stability of the aromatic structure, the planarity of the ring, and consequently the electronic distribution around the atoms.

1- Electrochemical measurements:

1-a Potentiodynamic behavior investigation

However, thiophene compounds have not been investigated extensively for their potential application as corrosion inhibitors for metal or alloys. This part of the present work investigates the electrochemical behavior of stainless steel electrode in the presence of different concentrations of the above thiophene compounds in acidic and chloride-containing acidic solutions.

- Potentiodynamic polarization experiments of stainless steel type 316 in 1.0 M H₂SO₄ at 25 °C in absence (a) and presence (b) of 2-
thiophene carboxylic hydrazide is depicted in Figure 2. The following observations could be drawn from the data shown in Figure 1.

The general shape of the potentiodynamic curve in the absence and presence of the inhibitor is comparable. However, the linear anodic and cathodic Tafel regions appeared extended over wider current range in the presence of the inhibitor when compared to that in the absence of the inhibitor.

The calculated corrosion potential, \(E_{corr}\), in the case of the curve (b) in presence of the inhibitor is \(-299.2\) mV with an associated corrosion current, \(i_{corr}\), of \(7.37 \times 10^{-5} \) A.cm\(^{-2}\). The corresponding values in the absence of the inhibitor are \(-1.0\) mV and \(1.385 \times 10^{-3}\) A.cm\(^{-2}\), respectively. The comparison of the values of \(E_{corr}\) and \(i_{corr}\) indicated that the addition of the 2-thiophene carboxylic hydrazide resulted in the shift of the corrosion potential to a negative value and a decrease in the corrosion current density.

The inhibitor appeared to be of the mixed type. This observation was withdrawn by comparing the values of the anodic and cathodic Tafel constants, \(\beta_a, \beta_c\). The values are 153.7, 145.0 mV/decade, and 46.4, 86.0 mV/decade in absence and presence of the inhibitor, respectively.

It was also concluded that the inhibitor acts as a mixed inhibitor for all
Figure 1 Potentiodynamic Polarization Curve of Stainless Steel Type 316 in 1.0 M H₂SO₄ in Presence and Absence of Thiophene Carboxylic Hydrazide
concentrations of solutions-containing chloride in which the stainless steel was examined as will be shown later.

The potentiodynamic curve was characterized by the appearance of well-defined anodic peak that appeared at +108.1 mV, which corresponds to an anodic peak current of $6.21 \times 10^{-3} \text{ A.cm}^{-2}$ in absence of the inhibitor. On the other hand the corresponding values of the anodic peak that appeared in the presence of TCH are $-200.5 \text{ mV}$ and $7.8 \times 10^{-3} \text{ A.cm}^{-2}$.

The anodic peak in both curves was followed by a slight increase in the current value and finally an almost constant value of the current. Oxygen evolution was not noticed as the potential exceeded the value of 1.0 V vs. Ag/AgCl.

In all cases, an ill-defined peak was observed in the active-passive region.

The polarization resistance values, calculated from the potentiodynamic curve were $2.340 \times 10^1$ and $1.777 \times 10^2 \text{ ohm.cm}^2$ for the non-inhibited solution and the inhibited one, respectively. The corresponding calculated corrosion rates are $1.269 \times 10^3$ and $6.755 \times 10^1 \text{ MPY}$, respectively. A reduction of ca. 94.67% in the rate of corrosion of the
nhibited stainless steel in the 1.0 M H\textsubscript{2}SO\textsubscript{4} solution is therefore observed when compared to the non-inhibited one.

The presence of stainless steel 316 in sulfuric acid has evidently a detrimental effect on the integrity of the surface. The addition of 2-thiophene carboxylic hydrazide showed to minimize the corrosion rate of the steel. At this stage of the work, it was necessary to explore two factors: (i) the effect of addition of chloride ion to examine the inhibitory efficiency of the thiophene derivative in presence of an aggressive anion and (ii) the effect of changing the concentration of the inhibitors at fixed concentration of sulfuric acid.

1-b Effect of Adding Chloride Ions in Presence and Absence of the Inhibitor:

Sodium chloride with concentration of 0.01 M was added to the acidic solution to form a concentration ratio of H\textsubscript{2}SO\textsubscript{4}/NaCl of 10/1. The following treatment of the results is based on comparing the results obtained from the potentiodynamic experiments of the stainless steel in presence and absence of 1.0 x 10\textsuperscript{-2} M thiophene carboxylic hydrazide.

Potentiodynamic polarization experiments of stainless steel in 0.01 M NaCl/0.1 M H\textsubscript{2}SO\textsubscript{4} at 25 °C in absence (a) and presence (b) of 1.0 x 10\textsuperscript{-2} M
Figure 2 Potentiodynamic Polarization Curve of Stainless Steel Type 316 0.01 M NaCl/0.1 M H₂SO₄ in Presence and Absence of Thiophene Carboxylic Hydrazide
thiophene carboxylic hydrazide is depicted in Figure 2. The following observations could be withdrawn from the data shown in Figure 2:

The general shape of the potentiodynamic curve in the absence and presence of the inhibitor is comparable to those obtained in Figure 1 for stainless steel tested in 1.0 M H₂SO₄.

The linear anodic and cathodic Tafel regions are apparently the same as shown in Figures 3a and 3b, respectively. The anodic and cathodic parts of the Tafel region in presence of 2-thiophene carboxylic hydrazide showed however, extended linear region when compared to the non-inhibited solution.

The calculated corrosion potential, Eₗcorr, in the case of the curve (b) in presence of the inhibitor is −375.3 mV with an associated corrosion current, iₗcorr, of 2.820 x 10⁻⁵ A.cm⁻². The corresponding values in the absence of the inhibitor are −332.1 mV and 2.068 x 10⁻⁴ A.cm⁻², respectively. The comparison of the values of Eₗcorr and iₗcorr indicated that the addition of 2-thiophene carboxylic hydrazide resulted in a cathodic shift in the corrosion potential values as compared to the study made in 1.0 M H₂SO₄. Moreover, a decrease in the corrosion current density is still observed when 2-thiophene carboxylic hydrazide is present. The later resulted in a noticeable decrease in the
corrosion rate from 189.56 MPY to 25.85 MPY and an inhibition efficiency of 86.36%.

Tafel slopes (β_c/β_a) for the cathodic and anodic processes exhibited lower values upon the addition of the 2-thiophene carboxylic hydrazide, namely, 83.4/65.7 mV/Decade in presence as compared to 119.5/82.0 mV/Decade in absence of inhibitor. The values are relatively lower than those cited in the literature for stainless steel 304 [76].

Electrode surface developed observable pits after polarization experiment.

Effect of Varying the Concentration of the Inhibitor

The effect of varying the concentration of the inhibitor with fixed concentration of sulfuric acid, ca. 0.5 M, on the corrosion of stainless steel examined in this section for two thiophene derivatives. The polarization curves for these solutions are shown in figures 4 and 5 in presence/absence 3-thiophene carboxyldehyde and 2-acetyl thiophene at room temperature (°C), respectively. The following observations could be concluded when comparing the data shown in figures 3 and 4:

The potentiodynamic curves exhibited distinct features when changing the type of inhibitor used. Thus, as the concentration of 3-
thiophene acetaldehyde in the medium increases the corrosion potential, $E_{\text{corr}}$, shifted to relatively higher cathodic values. On the other hand the corrosion potential remained basically constant in the case of using 2-acetyl thiophene.

An anodic peak is observed immediately after the extended anodic Tafel line for which the corresponding peak current and peak potential values changed upon changing the concentration of the inhibitor. In general, the peak current values shifted to lower values and that of the peak potential values shifted to relatively more positive values. These effects were more pronounced in the case of using 3-thiophene carboxaldehyde.

The inhibition efficiency increased as the concentration of the inhibitor increases. This is clearly shown when examining the values of the polarization resistance, $R_p$, and the corresponding corrosion rates calculated as depicted in tables 1 and 2, respectively. However, the inhibition efficiency for 3-thiophene carboxyldehyde is higher than that of 2-acetyl thiophene.

Again, it is important to notice that unexpectedly the values of the Tafel constants ($\beta_a$ and $\beta_c$), namely the anodic slope, are relatively lower than those cited in the literature [76]. Moreover, the addition
of the inhibitor to the medium changed both values of $\beta_a$ and $\beta_c$. This indicates that these inhibitors are of the mixed types as mentioned earlier in this section.

The potentiodynamic anodic plot is practically useful to determine important information such as: (i) the ability of the material to spontaneously passivate in the particular medium, (ii) the potential region over which the specimen remains passive, and (iii) the corrosion rate in the passive region. Anodic and cathodic Tafel slopes will be used to calculate the corrosion rate using the linear polarization method. The anodic or cathodic Tafel plots are described by the Tafel equation [4]:

$$\eta = \beta \log \frac{i}{i_{CORR}}$$  \hspace{1cm} (1)

Where,

$\eta$ = overvoltage, or the difference between the potential of the specimen and the corrosion potential.

$\beta$ = Tafel constant (slope).

$i_{CORR}$ = current at overvoltage $\eta$.

Rearranging equation (1) gives:

$$\eta = \beta (\log i - \log i_{CORR})$$  \hspace{1cm} (2)
Figure 3: Potentiodynamic curves for 316 stainless steel in absence and presence of 2-Thiophene acetyl
Figure 4: Potentiodynamic Curve of Stainless Steel Type 316 in 0.5 M H₂SO₄ in Presence and Absence of 3-Thiophene carboxaldehyde
### Table 1. Electrochemical Parameters For Stainless Steel Type 316 in 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 3- Thiophene carboxaldehyde

<table>
<thead>
<tr>
<th>[Inhibitor]$^*$ mol/L</th>
<th>E (mV)</th>
<th>$\beta_c$ mV/Decade</th>
<th>$\beta_a$ mV/Decade</th>
<th>$R_p$ (ohm.cm$^2$) $\times 10^2$</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eoc(V)</td>
<td>$E_{cor}$</td>
<td></td>
<td>Tafel</td>
<td>B</td>
</tr>
<tr>
<td>5 ml ethanol + 45 ml 0.5 sulfuric acid</td>
<td>-0.388</td>
<td>-348.1</td>
<td>88.1</td>
<td>55.4</td>
<td>1.640</td>
</tr>
<tr>
<td>5 x 10$^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.362</td>
<td>-291.9</td>
<td>112.6</td>
<td>30.9</td>
<td>3.95</td>
</tr>
<tr>
<td>1 x 10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.328</td>
<td>-343.5</td>
<td>78.6</td>
<td>99.8</td>
<td>32.39</td>
</tr>
</tbody>
</table>

### Table 2. Electrochemical Parameters For Stainless Steel Type 316 in 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 2-Acetyl Thiophene

<table>
<thead>
<tr>
<th>[Inhibitor]$^*$ mol/L</th>
<th>E (mV)</th>
<th>$\beta_c$ mV/Decade</th>
<th>$\beta_a$ mV/Decade</th>
<th>$R_p$ (ohm.cm$^2$) $\times 10^2$</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eoc(V)</td>
<td>$E_{cor}$</td>
<td></td>
<td>Tafel</td>
<td>B</td>
</tr>
<tr>
<td>5 ml ethanol + 45 ml 0.5 sulfuric acid</td>
<td>-0.388</td>
<td>-348.1</td>
<td>88.1</td>
<td>55.4</td>
<td>1.640</td>
</tr>
<tr>
<td>5 x 10$^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.382</td>
<td>-345.1</td>
<td>76.2</td>
<td>56.3</td>
<td>4.336</td>
</tr>
<tr>
<td>1 x 10$^{-2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.371</td>
<td>-343.1</td>
<td>70.5</td>
<td>77.1</td>
<td>19.84</td>
</tr>
</tbody>
</table>

59
This equation has the form $y = mx + b$, so a plot of $\eta$ vs. log $i$ is a straight line with slope $\beta$. As could be noticed from equation (2), when $\eta = 0$ (at $\Xi_{\text{CORR}}$), $\log \frac{i}{i_{\text{CORR}}} = 0$, $i/i_{\text{CORR}} = 1$, and $i = i_{\text{CORR}}$. The anodic and cathodic Tafel constants are used to calculate the corrosion rate from polarization measurement data according to the following equations:

\[
\frac{\Delta E}{\Delta i} = \frac{\beta_a \beta_c}{2.3(i_{\text{corr}} \beta_a + \beta_c)}
\]  

(3)

Where $\Delta E/\Delta i = \text{slope of the polarization resistance plot}$, where $\Delta E$ is expressed in volts and $\Delta i$ is expressed in $\mu$A. $\beta_a$, and $\beta_c$ are anodic and cathodic Tafel constants, respectively. The values of the Tafel constants are determined from the Tafel plot. $I_{\text{corr}}$ being the corrosion current in $\mu$A. Rearranging equation (3) yields:

\[
i_{\text{CORR}} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \frac{\Delta i}{\Delta E}
\]  

(4)

Therefore, the corrosion current can be related directly to the corrosion rate through the following equation:

\[
\text{Corrosion rate (mpy)} = \frac{0.13 i_{\text{corr}} (E.W.)}{d}
\]

(5)

E.W. = equivalent weight of the corroding species, g.

d = density of the corroding species, g/cm$^3$. 
\( i_{\text{corr}} = \) corrosion current density, \( \mu A/cm^2 \).

The inhibition efficiency \((P)\) is given by the following relation:

\[
P = \left( \frac{i_{\text{corr(un.)}} - i_{\text{corr(inh.)}}}{i_{\text{corr(un.)}}} \right) \times 100 \tag{6}
\]

**1-d Effect of Varying the Concentration of Sulfuric Acid on the Efficiency of Inhibition**

Polarization data for inhibited and uninhibited stainless steel 316 in 0.1 M, 0.5 M, and 1.0 M sulfuric acid solutions, are given in table 3. Anodic and cathodic Tafel slopes were reported in the range \( \beta_a / \beta_c = 121/87.5 \) to \( 169/106 \) [42, 44]. A slight difference is clearly observed in this study that indicates a change in the mechanism of inhibition for the thiophene derivatives when compared to those investigated previously.

As mentioned in preceding section, the thiophene derivatives appeared to act as mixed inhibitors. This observation was again proved when comparing the values of the anodic and cathodic Tafel constants \((\beta_a / \beta_c)\) such as in the case of applying 2-thiophene carboxylic hydrazide (c.f. table 3). The values are: 58.3/106.2 mV/decade, and 88.9/76.9 mV/decade in absence and presence of \( 1.0 \times 10^{-2} \) M 2-thiophene carboxylic hydrazide/0.1 M \( \text{H}_2\text{SO}_4 \), respectively. Two observations are worthwhile
mentioning: first, the values of the cathodic Tafel constant, $\beta_c$, calculated are generally smaller than those obtained for the uninhibited solutions in all concentrations $\text{H}_2\text{SO}_4$ studied. The values of the anodic Tafel constant, $\beta_a$, showed a general decrease in their values for the inhibited solutions with 2-thiophene carboxylic hydrazide compared to the uninhibited ones. Figure 5 shows the polarization curves for the inhibited stainless steel in different concentrations of sulfuric acid.

The polarization resistance values calculated from the potentiodynamic curve were $4.56 \times 10^2/5.39 \times 10^2$, $4.9 \times 10^3/2.70 \times 10^2$, $2.55 \times 10^1/2.68 \times 10^2$ ohms for the uninhibited solutions and the inhibited ones with different concentrations of $\text{H}_2\text{SO}_4$, respectively. The corresponding calculated corrosion rates are $0.834/0.772$, $0.528/0.969$, and $19.47/1.02$ MPY, respectively. Again, a reduction of up to about 94.74% in the rate of corrosion of the inhibited stainless steel in the 1.0 M sulfuric acid solution is therefore observed when compared to the non-inhibited one. The corrosion rate observed in the more concentrated solution was however, relatively higher than those found in the less concentrated acid solution. Exception was observed in the case of $\text{H}_2\text{SO}_4$ with concentration of 0.5 M, in which the stainless steel surface exhibited a peculiar trend.
<table>
<thead>
<tr>
<th>mol/L</th>
<th>mV/Decade</th>
<th>mV/Decade</th>
<th>(milliamp.)</th>
<th>X 10^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H₂SO₄</td>
<td>-352.2</td>
<td>-348.5</td>
<td>106.2</td>
<td>58.3</td>
</tr>
<tr>
<td>0.1 M H₂SO₄ + 10² M TCH</td>
<td>-394.1</td>
<td>-403.5</td>
<td>76.9</td>
<td>88.9</td>
</tr>
<tr>
<td>0.5 M H₂SO₄</td>
<td>-214.1</td>
<td>-215.7</td>
<td>342.7</td>
<td>1013.0</td>
</tr>
<tr>
<td>0.5 M H₂SO₄ + 10² M TCH</td>
<td>-315.4</td>
<td>-323.8</td>
<td>78.7</td>
<td>38.7</td>
</tr>
<tr>
<td>1.0 M H₂SO₄</td>
<td>-15.6</td>
<td>-1.0</td>
<td>112.0</td>
<td>87.8</td>
</tr>
<tr>
<td>1.0 M H₂SO₄ + 10² M TCH</td>
<td>-21.5</td>
<td>-17.1</td>
<td>104.5</td>
<td>36.9</td>
</tr>
</tbody>
</table>

Table 3  Electrochemical Parameters For Stainless Steel Type 316 in Different concentration of sulfuric acid in presence of 1X10⁻² M TCH, Data Derived form Potentiodynamic measurements.
Figure 5. Potentiodynamic curves for 316 stainless steel in different acid concentrations in presence of $1 \times 10^{-2}$ M 2-Thiophene carboxylic hydrazide
Thus, in the uninhibited solution, the electrode did not show a passive peak current when compared to the electrode examined in the 0.1 M and 1.0 M solutions, respectively. However, the presence of the inhibitor led to the formation of a passive peak in all concentrations. At this stage the value of corrosion rate in presence of the 2-thiophene carboxylic hydrazide in 0.5 M H₂SO₄ cannot be compared to the uninhibited solution. This concentration of sulfuric acid, ca. 0.5 M, appeared to be critical to the formation of the passive layer that appeared to be destabilized at the surface [78].

Examination of the surface of stainless steel electrode after exposure to different concentrations of sulfuric acid solutions (c.a. 0.1, 0.5 and 1.0 M) did not show eye-detectable pitting. However, the solution became reddish-brown coloration after polarization experiment. Detailed description of the surface morphology of the electrode will be given in the surface study section.

2 Effect of Molecular Structure on the Efficiency of Thiophene Derivatives Used for Corrosion Inhibition in Sulfuric Acid

The relationship between the structure of the inhibitor molecule and its efficiency has been the subject of several investigations [37, 38, 43, 44]. However, much less attention has been paid to the dependence of percentage
inhibition efficiency on the size and electronic distribution in the inhibitor molecule at the stainless steel surfaces. In this part of the present investigation, the candidate will attempt to answer few questions such as:

(i) What is the effect of changing the functional group in the side chain of the thiophene derivative on the percent inhibition efficiency?

(ii) What is the relation between the structure of the inhibitor molecules studied and their inhibition efficiencies?

(iii) What is the effect of changing the inhibitor on the mechanism of corrosion?

Figure 7 lists the compounds used in this study (cf. Figure 1 for structural formula). Energy minimization was used in order to display the compounds in three-dimensional format. Moreover, figure 6 reveals the electronic-density distribution profile for these compounds. From figures 1 and 6, one should be able to conclude the main criterion for the selection of the compounds studied that provided a number of variables. The variables considered in this study are:

(i) The effect of changing the position of substitution in the thiophene ring,

(ii) The change of type of substitution in the ring,

(iii) The change in the degree of functionality within the ring.
Both polarization resistance curves and Tafel plots for stainless steel in sulfuric acid in absence/presence of different thiophene derivatives with different concentrations are given in figures 7a, 7b, 8a, 8b, 9a, 9b, 10a, and 0b, respectively. The electrochemical parameters derived from the above mentioned polarization measurements are listed in tables 4a, 4b, 4c and 4d, respectively.

The data depicted in tables 4a-4d show that the inhibition efficiencies of different thiophene derivatives is still pronounced even at relatively low concentrations of the inhibitor used. However, the values of the inhibition efficiency increase as the concentration of sulfuric acid increases (as shown before) and as the concentration of the inhibitor increases. It could be noticed that the values of the anodic and cathodic Tafel constants ($\beta_a$ and $\beta_c$), generally showed the same trend observed with 2-thiophene carboxylic hydrazide for all other inhibitors studied. The values of the anodic and cathodic Tafel constants ($\beta_a$ and $\beta_c$) generally decrease upon addition of inhibitor and start to increase again with irregularity after a critical concentration of the inhibitor is reached [36, 38]. It is recognized that the inhibitors that shift the entire current-potential curves towards more negative (cathodic) values are cathodic-type inhibitors while those that shift the curves in the anodic direction are anodic-type inhibitors [79].
Figure 6. Conformation of Inhibitors
Table 4a  Electrochemical Parameters For Stainless Steel Type 316 in 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 2-Thiophene Carboxylic Hydrazide.

<table>
<thead>
<tr>
<th>[Inhibitor]</th>
<th>E (mV)</th>
<th>βc (mV/Decade)</th>
<th>βa (mV/Decade)</th>
<th>Rp (ohm.cm²) x 10²</th>
<th>B</th>
<th>Icorr (A.cm²) x 10⁻⁴</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.461</td>
<td>462.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>-0.359</td>
<td>-353.9</td>
<td>92.6</td>
<td>58.7</td>
<td>1.174</td>
<td>1.187</td>
<td>15.6</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>-0.367</td>
<td>-357.4</td>
<td>86.6</td>
<td>58.4</td>
<td>1.684</td>
<td>1.241</td>
<td>15.1</td>
</tr>
<tr>
<td>5 x 10⁻³</td>
<td>-0.359</td>
<td>-340.3</td>
<td>92.2</td>
<td>49.7</td>
<td>1.93</td>
<td>1.141</td>
<td>14.0</td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>-0.349</td>
<td>-349.0</td>
<td>92.7</td>
<td>52.2</td>
<td>17.7</td>
<td>1.531</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Table 4b  Electrochemical Parameters For Stainless Steel Type 316 in 7 ml ethanol and diluted with 43ml Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 2-Thiophene Carboxylic acid.

<table>
<thead>
<tr>
<th>[Inhibitor]</th>
<th>E (mV)</th>
<th>βc (mV/Decade)</th>
<th>βa (mV/Decade)</th>
<th>Rp (ohm.cm²) x 10²</th>
<th>B</th>
<th>Icorr (A.cm²) x 10⁻⁴</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.420</td>
<td>-419.6</td>
<td>120.1</td>
<td>88.9</td>
<td>0.8269</td>
<td>0.3458</td>
<td>22.18</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>-0.396</td>
<td>-414.3</td>
<td>81.6</td>
<td>54.4</td>
<td>6.87</td>
<td>0.9042</td>
<td>15.48</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>-0.382</td>
<td>-406.0</td>
<td>80.6</td>
<td>46.9</td>
<td>10.1</td>
<td>1.416</td>
<td>13.66</td>
</tr>
<tr>
<td>5 x 10⁻³</td>
<td>-0.404</td>
<td>-417.6</td>
<td>83.5</td>
<td>60.1</td>
<td>1.65</td>
<td>0.8077</td>
<td>16.49</td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>-0.385</td>
<td>-396.9</td>
<td>78.0</td>
<td>55.5</td>
<td>2.27</td>
<td>1.39</td>
<td>15.17</td>
</tr>
</tbody>
</table>
Table 4c  Electrochemical Parameters For Stainless Steel Type 316 in 5 ml ethanol and diluted with 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 3- Thiophene carboxaldehyde.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>( E (mV) )</th>
<th>( \beta_c ) (mV/Decade)</th>
<th>( \beta_a ) (mV/Decade)</th>
<th>( \beta_T ) (ohm.cm(^2)) ( \times 10^2 )</th>
<th>( B )</th>
<th>( I_{corr} ) (A.cm(^{-2})) ( \times 10^{-4} )</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.404</td>
<td>-386.2</td>
<td>127.0</td>
<td>131.3</td>
<td>0.76</td>
<td>1.098</td>
<td>28.06</td>
</tr>
<tr>
<td>5 x 10(^{-4})</td>
<td>-0.391</td>
<td>-366.7</td>
<td>93.8</td>
<td>38.3</td>
<td>4.353</td>
<td>1.252</td>
<td>11.82</td>
</tr>
<tr>
<td>1 x 10(^{-3})</td>
<td>-0.387</td>
<td>-365.3</td>
<td>83.3</td>
<td>42.9</td>
<td>3.23</td>
<td>1.896</td>
<td>12.3</td>
</tr>
<tr>
<td>5 x 10(^{-3})</td>
<td>-0.358</td>
<td>-336.4</td>
<td>77.6</td>
<td>28.3</td>
<td>16.4</td>
<td>4.771</td>
<td>9.016</td>
</tr>
<tr>
<td>1 x 10(^{-2})</td>
<td>-0.346</td>
<td>-335.6</td>
<td>81.3</td>
<td>40.3</td>
<td>22.8</td>
<td>8.38</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Table 4d  Electrochemical Parameters For Stainless Steel Type 316 in 5 ml ethanol and diluted with 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 2-Acetyl Thiophene.

<table>
<thead>
<tr>
<th>[Inhibitor]</th>
<th>( E (mV) )</th>
<th>( \beta_c ) (mV/Decade)</th>
<th>( \beta_a ) (mV/Decade)</th>
<th>( \beta_T ) (ohm.cm(^2)) ( \times 10^2 )</th>
<th>( B )</th>
<th>( I_{corr} ) (A.cm(^{-2})) ( \times 10^{-4} )</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.381</td>
<td>-386.2</td>
<td>127</td>
<td>131.3</td>
<td>0.761</td>
<td>1.098</td>
<td>28.0</td>
</tr>
<tr>
<td>5 x 10(^{-4})</td>
<td>-0.3915</td>
<td>-369.7</td>
<td>96.4</td>
<td>55.2</td>
<td>1.998</td>
<td>1.30</td>
<td>15.2</td>
</tr>
<tr>
<td>1 x 10(^{-3})</td>
<td>-0.3919</td>
<td>-369.7</td>
<td>93.8</td>
<td>48.9</td>
<td>1.663</td>
<td>1.347</td>
<td>13.9</td>
</tr>
<tr>
<td>5 x 10(^{-3})</td>
<td>-0.3909</td>
<td>-354.4</td>
<td>109.3</td>
<td>53.2</td>
<td>2.093</td>
<td>1.44</td>
<td>15.5</td>
</tr>
<tr>
<td>1 x 10(^{-2})</td>
<td>-0.3859</td>
<td>-343.9</td>
<td>97.7</td>
<td>65.1</td>
<td>5.573</td>
<td>2.3</td>
<td>16.9</td>
</tr>
</tbody>
</table>
On the other hand, mixed-type inhibitors cause a shift in the cathodic Tafel lines towards more negative values and the current-potential curves near the free corrosion potential towards less cathodic potentials. In this respect, Tafel results for TCH showed a dramatic shift of the entire potential-current curves towards more cathodic values upon addition of the inhibitor. On the other hand, values of the corrosion potential, $E_{\text{corr}}$, showed slight shift towards more anodic values upon increasing the concentration of TCH while the corresponding corrosion current, $i_{\text{corr}}$, decreased towards much lower values (cf. figure 7a and table 4a). Moreover, the values of the anodic Tafel constant, $\beta_a$, decreased from a value of 109.6 mV/Decade for the uninhibited solution to a value of $\sim$50.0 mV/Decade at higher concentrations of TCH. The corresponding values of the cathodic Tafel constant, $\beta_c$, showed a change in value from 117.0 mV/Decade to a value around 92.7 mV/Decade for all concentration studied of TCH. Polarization resistance data are depicted in figure 7b, and the corresponding electrochemical parameters are given in table 4a for TCH. Examination of figure 7b and table 4a revealed that the polarization resistance increased dramatically upon the addition of the inhibitor and resulted in a slight increase in the slope of the polarization resistance curve upon increasing the concentration of the inhibitor in solution.
Figure 7a. Tafel curves for 316 stainless steel in 0.5M of sulforic acid in absence and presence of thiophene carboxylic hydrazide
Figure 7b: Polarization curves for 316 stainless steel in different concentrations of TCH
Inhibition efficiency of 99.34% was reached when using a concentration of $1.0 \times 10^{-2}$ M of TCH. Figure 9a shows the Tafel curves for stainless steel in sulfuric acid in absence and presence of different concentrations of TCA. It could be observed that, a slight shift in the entire potential-current curves for stainless steel were observed upon addition of TCA to the acidic solution. Corrosion potential values, $E_{corr}$, showed slight shift towards anodic directions as in the case of TCH while the corrosion current values, $i_{corr}$, changed differently in this case. Thus, a decrease in $i_{corr}$ was observed upon addition of TCA that reached a limiting value at the concentration of $1.0 \times 10^{-3}$ M, and started to increase as the concentration of TCA reached $1.0 \times 10^{-2}$ M. The values of the anodic Tafel constant, $\beta_a$, decreased from a value of 88.9 mV/Decade for the uninhibited solution to a value of ~55.5 mV/Decade at higher concentrations of TCA. The corresponding values of the cathodic Tafel constant, $\beta_c$, showed a change in value from 120.1 mV/Decade to a value around 78.0 mV/Decade for all concentration studied of TCA. Polarization-resistance experiments (cf. figure 8b and table 4b) and corrosion rate calculations revealed that at the concentration of $1.0 \times 10^{-3}$ M TCA, minimal corrosion rate as well as maximum polarization resistance are achieved. This interesting observation could be explained on the basis that a critical concentration of TCA is reached in solution that caused optimal
Figure 8a: Tafel curves for 316 stainless steel in 0.5 M of sulfuric acid in absence and presence of 2-Thiophene carboxylic acid.
Figure 8b. Polarization curves for 316 stainless steel in absence and presence of 2-Thiophene Carboxylic Acid
inhibition efficiency for a particular concentration of the acid. Similar observations were cited earlier in the literature for other sulfur-containing compounds [38, 80]. Above the optimal concentration, TCA eventually stimulate, rather than increase the inhibition efficiency. It was mentioned earlier that at low concentrations of sulfur-containing inhibitors, surface coverage of the adsorbed molecules is too low to result in efficient coverage to prevent corrosion of the stainless steel [42]. Moreover, some authors [81, 82] attributed this phenomenon to the hydrolysis of the sulfur-compounds to produce corrosion promoting species, such as HS\(^-\) and S\(^2-\). Hydrolysis is only acceptable to take place in fairly concentrated solutions where the equilibrium constant of the protonated species of these compounds has to be taken into account. Another plausible mechanism for the observed results at a particular concentration of the inhibitor could be explained on the basis of increasing the acidity of solution via the carboxylic functionality of the inhibitor above 1.0 x 10\(^{-3}\) M value. Thus, exceeding this magic concentration of TCA results in two opposing effects, the first is increasing the inhibition efficiency and the second being the increase in the total acidity of the solution.

Figure 9a shows the Tafel curves for stainless steel in sulfuric acid in absence and presence of different concentrations of TCAL. \(E_{\text{corr}}\) values
show similar trend as that observed in the case of TCA. However, the trend observed for the Tafel constants displayed some differences. On the other hand, the values of $i_{\text{corr}}$ exhibited a gradual decrease in value with increase in concentration of the inhibitor. Thus, the values of the anodic Tafel constant, $\beta_a$, decreased from a value of 131.3 mV/Decade for the uninhibited solution to a value of ~40.3 mV/Decade at higher concentrations of TCAL. The corresponding values of the cathodic Tafel constant, $\beta_c$, showed a change in value from 127.0 mV/Decade to a value around 81.3 mV/Decade for all concentration studied of TCAL (cf. table 4c). Polarization resistance measurements data are depicted in figure 9b. The data clearly exhibited an expected trend of increase in the slope of the E-I with increase in the concentration of the inhibitor added. Figure 11a depicts the data obtained for the Tafel measurements at stainless steel in sulfuric acid in absence and presence of different concentrations of AcT. The corresponding electrochemical data are displayed in table 4d. As could be noticed from figure 10a, the entire potential-current curves are shifted towards more anodic values. Moreover, both anodic and cathodic Tafel constants showed changes towards relatively lower values upon addition of AcT and upon increasing its concentration.
Figure 9a. Tafel curves for stainless steel 316 in 0.5M sulfuric in presence and absence of thiophene carboxaldehyde
Figure 9 b. Stainless Steel 316 in 0.5 M Sulfuric Acid in Presence and Absence of 3-Thiophene Carboxaldehyde
Figure 10a: Tafel curves for 316 in 0.5 M sulfuric acid in absence and present of 2-Acetyl Thiophene

- 0 inhibitor
- 5 X 10^{-4} M
- 1 X 10^{-3} M
- 5 X 10^{-3} M
- 1 X 10^{-2} M

Log I (A. cm^{-2})
Figure 10b. Polarization curves for 316 in 0.5 M sulfuric in presence and absence of acetyl thiophene
Thus, the values of the anodic Tafel constant, $\beta_a$, decreased from a value of -1.3 mV/Decade for the uninhibited solution to a value of $\sim$65.1 mV/Decade at higher concentrations of AcT. The corresponding values of the cathodic Tafel constant, $\beta_c$, showed a change in value from 127 V/Decade to a value around 97.7 mV/Decade for all concentration studied except for the concentration of $5 \times 10^{-3}$ M that showed a value of 109 V/Decade. However, the change in the slope of the anodic Tafel constant more pronounced when increasing the concentration of this inhibitor when compared to the corresponding values of the cathodic Tafel constant.

Results for the polarization resistance measurements are shown in figure b. Again, similar trend of increase in the slopes of the $E$-$\log \text{ concentration}$ curves with concentration of the inhibitor is still observed as in the case of other inhibitors studied.

Figure 11 shows the variation of the corrosion rate and inhibition efficiency percentage with concentration. The results indicate that the factors influencing the inhibition efficiency could be summarized as follows:

(i) The order of stability of the thiophene derivatives in solution and consequently their tendency to adsorb at the stainless steel surface.
Figure 11. Variation Rate and % Inhibition Efficiency
(ii) The position of the substitution on the ring.

(iii) The number and the nature of substituent (degree of functionality).

Thus, the order of percentage inhibition efficiency was TCH > TCA > TCAL > AcT. The explanation of this order in reference to the above factors and molecular structure consideration could be as follows: the structure of the four thiophene derivatives posses a common part of the structure, that is the thiophene moiety attached the C=O group. However, substitution in TCAL is at the 3-position when compared to the other inhibitors. The lone pairs on the two nitrogen atoms of TCH are delocalized and consequently will cause the structure to be stabilized. The stabilization energy resulted in the case of TCH in enhancing the surface coverage over the stainless steel through sulfur atom anchoring around which the electron density is increased [81, 82]. Therefore, surface coverage in this case is expected to increase and is illustrated in an increase in corrosion inhibition efficiency. Similar argument could be put forward in the case of TCA at relatively low concentrations. However, as the concentration of TCA increases in solution, the local acidity at the surface of stainless steel increases as well. This later effect results in two competitive events, the first is inhibition through surface coverage and the second is enhancement to the dissolution (corrosion) at the initial stage of the anodic Tafel portion as
indicated in the I-E curve. The results indicated that TCAL exhibited a regular increase in the percentage of inhibition efficiency that reached a stable value at the higher concentration. The leveling in the inhibition efficiency could be explained from the fact of the possible formation of thin polymeric layer at the surface of the stainless steel due to the polymerization of TCAL [83]. On the other hand, AcT exhibited the least percentage in inhibition efficiency. This could be explained in terms of the lack of presence of lone pairs on the methyl group for AcT when compared to other compounds.

**Temperature Coefficient of Corrosion Inhibition of Stainless Steel by Thiophene Carboxaldehyde**

The corrosion of stainless steel 316 in 0.5 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of different concentrations of thiophene carboxaldehyde (5.0 x 10<sup>-4</sup>-1.0 x 10<sup>-2</sup> M) at different temperatures (25-40 °C) was studied using Tafel and linear polarization experiments. The percentage inhibition efficiency was calculated using equation (6). Figure 12 shows the plot of the protection efficiency against the logarithm of concentration of TCAL at different temperatures. Inspection of the data depicted in figure 12 reveals that the extent of protection efficiency increases with the concentration of
the inhibitor as mentioned before. On the other hand, it was found that the inhibition protection efficiency decreases with increasing the temperature. Moreover, it could be noticed that the curves possess a characteristic s-shaped isotherms for some concentrations of the acid used, that indicate an adsorption mechanism for the inhibition process. General irregularity could be observed at some concentrations for different temperatures. The studied inhibitor is a five-member heterocycle ring with either half-chair or envelope-like structures [84, 85] with the most probable structure in the half-chair form. The adsorption may be mainly via the lone-pair of the sulfur-atom in the ring while the rest of the molecule covers the surface in the case of TCAL. Some interaction of the electron cloud of the ring could also be expected along with water displacement from the surface as indicated previously by Hubbard et al. [86]. The resulting mode of coverage of the inhibitor to the surface would be an anchor (through the sulfur atom) and a blanket (from the rest of the molecule). Different adsorption isotherms were suggested in the literature [85 – 87] and were tested for their fit to the experimental data. The degree of coverage, $\theta$, at constant potential is given by the following relation [88, 89]:

$$\theta = 1 - \frac{i_c}{i_s}$$ (7)
Table 5a. Electrochemical Parameters For Stainless Steel Type 316 in 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 2-Thiophene Carboxaldehyde at 25° C.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>E (mV)</th>
<th>Eoc</th>
<th>Ecor</th>
<th>B</th>
<th>Rp(ohm.cm²) x 10²</th>
<th>B</th>
<th>Icorr (A.cm⁻²) x 10⁻⁴</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-0.404</td>
<td>-386.0</td>
<td>127</td>
<td>131.3</td>
<td>0.76</td>
<td>1.098</td>
<td>28.06</td>
<td>3.683</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>-0.368</td>
<td>-339.4</td>
<td>93.8</td>
<td>38.3</td>
<td>2.53</td>
<td>1.252</td>
<td>11.82</td>
<td>0.262</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>-0.387</td>
<td>-365.3</td>
<td>86.8</td>
<td>40.2</td>
<td>3.069</td>
<td>1.896</td>
<td>12.3</td>
<td>0.388</td>
</tr>
<tr>
<td>5 x 10⁻³</td>
<td>-0.358</td>
<td>-336.4</td>
<td>77.6</td>
<td>28.3</td>
<td>16.4</td>
<td>4.771</td>
<td>9.016</td>
<td>0.0548</td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>-0.346</td>
<td>-335.6</td>
<td>81.3</td>
<td>40.3</td>
<td>22.8</td>
<td>8.38</td>
<td>11.7</td>
<td>0.0511</td>
</tr>
</tbody>
</table>

Table 5b. Electrochemical Parameters For Stainless Steel Type 316 in 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 2-Thiophene Carboxaldehyde at 30° C

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>E (mV)</th>
<th>Eoc</th>
<th>Ecor</th>
<th>B</th>
<th>Rp(ohm.cm²) x 10²</th>
<th>B</th>
<th>Icorr (A.cm⁻²) x 10⁻⁴</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-0.327</td>
<td>-325.5</td>
<td>78.1</td>
<td>40.1</td>
<td>1.11</td>
<td>1.241</td>
<td>11.5</td>
<td>1.16</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>-0.336</td>
<td>-321.7</td>
<td>90.1</td>
<td>38.2</td>
<td>2.49</td>
<td>1.137</td>
<td>11.6</td>
<td>0.467</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>-0.335</td>
<td>-310.5</td>
<td>87.1</td>
<td>30.5</td>
<td>3.09</td>
<td>1.550</td>
<td>9.82</td>
<td>0.316</td>
</tr>
<tr>
<td>5 x 10⁻³</td>
<td>-0.313</td>
<td>-283.1</td>
<td>101.0</td>
<td>20.4</td>
<td>3.56</td>
<td>2.80</td>
<td>7.37</td>
<td>0.206</td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>-0.297</td>
<td>-274.8</td>
<td>94.5</td>
<td>28.8</td>
<td>7.92</td>
<td>5.773</td>
<td>9.59</td>
<td>0.119</td>
</tr>
</tbody>
</table>
Table 5c. Electrochemical Parameters For Stainless Steel Type 316 in 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 2-Thiophene Carboxaldehyde at 35°C.

<table>
<thead>
<tr>
<th>[Inhibitor] \ mol/L</th>
<th>E (mV) ( E_{oc} )</th>
<th>( \beta_c ) mV/Decade</th>
<th>( \beta_a ) mV/Decade</th>
<th>( R_p ) (ohm.cm²) ( x 10^2 )</th>
<th>B ( \times 10^{-4} )</th>
<th>( I_{corr} ) (A.cm⁻²) ( x 10^{-4} )</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.340</td>
<td>111.3</td>
<td>85.3</td>
<td>0.866</td>
<td>20.3</td>
<td>2.4</td>
<td>221.8</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>-0.816</td>
<td>89.0</td>
<td>33.3</td>
<td>1.046</td>
<td>10.5</td>
<td>1.005</td>
<td>92.14</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>-0.811</td>
<td>93.2</td>
<td>32.1</td>
<td>1.295</td>
<td>10.3</td>
<td>0.800</td>
<td>73.38</td>
</tr>
<tr>
<td>5 x 10⁻³</td>
<td>-0.326</td>
<td>87.5</td>
<td>38.5</td>
<td>27.16</td>
<td>11.6</td>
<td>0.427</td>
<td>39.17</td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>-0.312</td>
<td>80.7</td>
<td>33.0</td>
<td>27.35</td>
<td>19.1</td>
<td>0.371</td>
<td>34.06</td>
</tr>
</tbody>
</table>

Table 5d. Electrochemical Parameters For Stainless Steel Type 316 in 0.5 M Sulfuric Acid Solutions in The Absence and Presence of Different Concentrations of 2-Thiophene Carboxaldehyde at 40°C.

<table>
<thead>
<tr>
<th>[Inhibitor] \ mol/L</th>
<th>E (mV) ( E_{oc} )</th>
<th>( \beta_c ) mV/Decade</th>
<th>( \beta_a ) mV/Decade</th>
<th>( R_p ) (ohm.cm²) ( x 10^2 )</th>
<th>B ( \times 10^{-4} )</th>
<th>( I_{corr} ) (A.cm⁻²) ( x 10^{-4} )</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.350</td>
<td>92.0</td>
<td>54.4</td>
<td>1.145</td>
<td>14.8</td>
<td>1.296</td>
<td>118.7</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>-0.344</td>
<td>97.2</td>
<td>43.3</td>
<td>1.250</td>
<td>13.0</td>
<td>1.040</td>
<td>95.30</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>-0.331</td>
<td>82.0</td>
<td>31.9</td>
<td>3.634</td>
<td>9.98</td>
<td>0.274</td>
<td>25.14</td>
</tr>
<tr>
<td>5 x 10⁻³</td>
<td>-0.325</td>
<td>90.2</td>
<td>24.29</td>
<td>2.047</td>
<td>8.3</td>
<td>0.404</td>
<td>37.04</td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>-0.300</td>
<td>96.3</td>
<td>20.30</td>
<td>5.365</td>
<td>7.28</td>
<td>0.136</td>
<td>12.61</td>
</tr>
</tbody>
</table>

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Where \( i_u \), \( i \) are the corrosion currents of uninhibited and inhibited experiments, respectively.

As was indicated above, the inhibition efficiency increases with concentration, however shows irregularities at some concentrations with temperature as indicated in figure 12. The latter is confirmed by inspecting the values of the Tafel constants listed in table 5a, 5b, 5c, and 5d, respectively. More interestingly, the values of the cathodic Tafel constant \( \beta_c \) that corresponds to hydrogen evolution in absence of inhibitor, decreased noticeably as the temperature increases from 25 to 30 °C. The value of \( \beta_c \) starts to increase again as the temperature increases above 30 °C. Bockris et al. [90], formalized a mechanism for hydrogen evolution reaction as \( \beta_c \) decreases with temperature. In this case, the mechanism seems to work similarly for lower temperatures and changes as the temperature increases. On the other hand, corresponding values of \( \beta_s \) showed similar trend as those for \( \beta_c \). The relatively lower values found in this study for the stainless steel compared to those found for mild steel [91] and iron [92], are due to less impurities present in stainless steel. Effective inhibition efficiency is, therefore, more pronounced at lower temperatures. The calculated protection efficiencies when using \( 5.0 \times 10^{-3} \) M TCAL are 77.2, 56.0, 51.7, 57.9 % in 0.5 M H\(_2\)SO\(_4\) at 25, 30, 35, and 40 °C, respectively.
Figure 12. Inhibition efficiency for different concentration of TCAL at different temperature.
We have noticed that the values of inhibition efficiencies calculated from linear polarization measurements are comparable to those estimated from the Tafel experiments. Other researchers mentioned similar findings earlier [93-95].

At this stage we are assuming that a layer of the thiophene inhibitor adsorbs onto the surface of the stainless steel. This later finding is confirmed by the surface reflectance FT-IR measurements shown in a later section. Therefore, the fraction of the surface covered by the inhibitor and not exposed to corrosion events is \( i_{\text{inh}} = \frac{i_{\text{inh}}}{i_{\text{uninh}}} \). The later assumption is only valid when complete coverage of the surface by the inhibitor is readily maintained at all temperature ranges study.

Figure 14 depicts the Langmuir adsorption isotherm relation given by the following [91]:

\[
\frac{\theta}{1 - \theta} = A \cdot C \cdot \exp\left(\frac{Q}{RT}\right) \tag{8}
\]

Where \( A \) is a constant, \( C \) is the inhibitor concentration, \( Q \) is the heat of adsorption, \( \theta \) is the part of surface covered by the inhibitor, and \( 1 - \theta \) is the vacant sites. The logarithmic format of equation (8) can be expressed as follows [91]:

\[
\log\left(\frac{\theta}{1 - \theta}\right) = \log A + \log C + \frac{Q}{2.3 RT} \tag{9}
\]
Thus, a plot of log $[\theta/(1-\theta)]$ vs. log $C$ should yield a straight line. As could be noticed from figure 14 that as the temperature reaches 40 °C, the change in surface coverage with change in temperature differs in magnitude and extent when compared to lower temperatures. A direct application of the Langmuir equation (9) is to plot values of log $[\theta/(1-\theta)]$ vs. $1/T$ at given concentration values. The heat of adsorption could be estimated for different concentrations as depicted in figure 15. The heats of adsorption are 83.18, -60.34, -131.63, and -116.47 for $5.0 \times 10^{-4}$, $1.0 \times 10^{-3}$, $5.0 \times 10^{-3}$, and $0 \times 10^{-2}$ M inhibitor, respectively. On the other hand, the heat of adsorption could be estimated from the relation between the rate of corrosion and the inverse of temperature [91]. In this method, the total measured rate of corrosion could be expressed as the sum of two rates, the first for the rate of uninhibited reaction, and the second for the rate of corrosion of completely covered surface. The expression of these two rates is [91]:

$$\frac{-d[Fe]}{dt} = K_1(1 - \theta) + K_2\theta$$  \hspace{1cm} (10)

Where $K_1$ and $K_2$ are the rate constants of the two processes, respectively.

In most of our discussion, we will be considering the Langmuir model of adsorption. Thus, from substituting for the values of $\theta$ from equation (8) into equation (10), we obtain:
\[ -\frac{d[Fe]}{dt} = \frac{K_1 A C e^{\frac{Q}{RT}}}{1 + A C e^{\frac{Q}{RT}}} + \frac{K_2 A e^{\frac{Q}{RT}}}{1 + A e^{\frac{Q}{RT}}} \]  \hspace{1cm} (11)

In equation (11), the activation energy should increase as the extent of inhibition increases. This is related to the term \(A C e^{\frac{Q}{RT}}\), and when the surface is inhibited, \(C\) is equal to zero. Upon rearrangement of equation (11), where \(K_1\) and \(K_2\) are replaced by their exponential forms:

\[ -\frac{d[Fe]}{dt} = \frac{K_1 e^{\frac{-E_1}{RT}}}{1 + A C e^{\frac{Q}{RT}}} + \frac{K_2 A C e^{\frac{Q}{RT} - \frac{E_1}{RT}}}{1 + A C e^{\frac{Q}{RT}}} \]  \hspace{1cm} (12)

In the later case, the activation energy for the corrosion process should be equal to \(E_1\). Moreover, as the extent of inhibition increases, and \(\theta\) becomes large, the activation energy increases to equal \((E_1 + Q)\). At very large values for \(\theta\) the activation energy is equal to \(E_2\). If we assume intermediate coverage by the inhibitor to the stainless steel surface and adopting the Langmuir model, the activation energy of adsorption could be determined.

In this respect, a plot of the rate of corrosion versus \(1/T\) as depicted in figure 15 would allow the calculation of activation energy of adsorption. The activation energy is then plotted versus the inhibitor concentration as shown in figure 16. The maximum value shown in figure 16 corresponds to the value of \((E_1 + Q)\) that is equal to \(120\) kJ.mol\(^{-1}\) for \(7 \times 10^{-3}\) mol.
Figure 13. Plot of Log $\theta/(1-\theta)$ vs. Log C for 316 stainless steel in presence of TCAL in 0.5 M H$_2$SO$_4$. 
Fig 14: Plots of Log(θ/1-θ) vs. 1/T at different concentrations of 3-Thiophene carboxaldehyde (1) 5 x 10^{-4}, (2) 1 x 10^{-3}, (3) 5 x 10^{-3}, (4) 1 x 10^{-2} in 0.5 M sulfuric acid.
If the $E_1$ for the uninhibited reaction is equal to 7.64 kJ.mol$^{-1}$ [96], therefore, the heat of adsorption is equal to 59.7 kJ.mol$^{-1}$. This value is reasonably agreeing with that obtained previously from the expression of equation (9).

From the aforementioned discussion, we can conclude that the inhibitor molecules are well adsorbed over the metal surface and that surface coverage of the stainless steel surface by the inhibitor change with temperature and concentration, respectively. In the case of lack of interaction between adsorbed inhibitor molecules at the surface, the Langmuir model suggests:

$$KC = \left[ \frac{\theta}{1 - \theta} \right]$$  \hspace{1cm} (13)

On the other hand, the thermodynamic parameters shown in table 6, were estimated from the following relations [91]:

$$\Delta G^* = -RT \ln(K \times 55.5)$$
$$\Delta H^* = \frac{R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \ln K(T_2)}{K(T_1)}$$  \hspace{1cm} (14)
$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T}$$

And the temperature coefficient could be estimated according to:

$$\Delta G = \Delta H - Z FT \left( \frac{dE}{dT} \right)$$  \hspace{1cm} (15)
\[ V_{\text{eff}} = -2.3 \times 8.314 \times \frac{d \log i}{d \log T} \]  

(15b)

As indicated in the values calculated in table 6, the enthalpy of adsorption, \( \Delta H^0 \), entropy of adsorption, \( \Delta S^0 \), and free energy of adsorption, \( \Delta G^0 \), are all negative. The negative value of \( \Delta H^0 \) indicates the adsorption process is exothermic. On the other hand, the magnitude of \( \Delta S^0 \) and \( \Delta G^0 \) indicate that replacement process took place during the adsorption of the inhibitor molecules at the surface of the stainless steel [97].

**4- Electrochemical Impedance Spectroscopy (EIS)**

The corrosion behavior of stainless steel 316, in acidic solution in the presence of 2-thiophene carboxylic acid and 2-acetyl thiophene with different concentrations was investigated by the EIS method at room temperature. The locus of Nyquist plots is regarded as one part of a semicircle. The equivalent circuit model employed for this system is as previously reported in the literature [98] and shown in figure 17. Nyquist plots of stainless steel 316 in inhibited and uninhibited acidic solutions containing various concentrations of TCAL and AcT are shown in figures 17 and 18. As could be noticed the impedance diagrams obtained are not perfect semicircles, and this could be attributed to frequency dispersion as indicated earlier [99]. The equivalent circuit to which the data were fitted is
Figure 15. Arrhenius plots of Inhibited Corrosion Rate for 3-Thiophene carboxaldehyde
Figure 16. Effective energy for inhibition corrosion of stainless steel in 0.5 M H₂SO₄ and TCAL.
<table>
<thead>
<tr>
<th>Temperature</th>
<th>ΔG (KJ/mol)</th>
<th>ΔH (KJ/mol)</th>
<th>ΔS (J/mol.K)</th>
<th>Temp.coeff. dE/dT</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>-26.610</td>
<td>-38.625</td>
<td>-39.652</td>
<td></td>
</tr>
<tr>
<td>40°C</td>
<td>-26.214</td>
<td></td>
<td></td>
<td>-2.05x10^7</td>
</tr>
</tbody>
</table>

Table 6: The thermodynamic parameters for the TCAL in 0.5 M H₂SO₄.
The charge-transfer resistance, $R_t$, values could be calculated from the difference in impedance at lower and higher frequencies. To obtain the double layer capacitance ($C_{dl}$), the frequency at which the imaginary component of the impedance is maximum ($-\text{Imag max}$) is found and $C_{dl}$ values could be calculated from the equation [99]:

$$f(-\text{Imag max}) = \frac{1}{2\pi C_{dl} R_t} \quad (16)$$

could be noticed from the data of figures 19 and 20 that the impedance semicircle size depends on type and concentration of the inhibitor used. The presence of the semicircle in the impedance diagrams indicated that, the corrosion of stainless steel 316 is, controlled by a charge transfer process. Tables 7 and 8 depict the impedance parameters obtained by line fitting to the semicircle. The charge transfer resistance ($R_{ct}$) increases as the concentration of the inhibitor increases for the two inhibitors studied. Also, the double layer ($C_{dl}$) decreases with increase in the concentration of the inhibitor. This decrease is due to adsorption of inhibitor on the metal surface causing a change of the double layer structure as indicated earlier [100]. When comparing the inhibition efficiencies obtained from testing methods used in this study, it can be concluded that there is a fair agreement between the obtained results from EIS and other d.c techniques. Again, it
could be noticed that 2-acetyl thiophene showed higher inhibition efficiency at lower concentrations when compared to 2-thiophene carboxylic that showed relatively higher inhibition efficiency for higher concentrations. In summary, all electrochemical techniques used in this study showed comparable trend in inhibition efficiency and that the formation of stable film through chemical/physical adsorption on stainless steel surface is responsible for the observed corrosion inhibition of the thiophene derivatives studied. It is worthwhile to mention that inhibition efficiency was calculated from EIS measurements as indicated in tables 7 and 8 using the following relation [100]:

$$ p = \frac{R_{ct(\text{uninh.})}^{-1} - R_{ct(\text{inh.})}^{-1}}{R_{ct(\text{uninh.})}^{-1}} \times 100 $$

(17)

Where $p$ is the inhibition efficiency, $R_{ct(\text{uninh.})}$ and $R_{ct(\text{inh.})}$ are the charge transfer resistance values without and with inhibitor, respectively. We have followed the progress of $R_{ct}$ and $C_{dl}$ with immersion time and noticed that without the inhibitor, $R_{ct}$ decreases with immersion time, whereas $C_{dl}$ increases. Both $R_{ct}$ and $C_{dl}$ change trend to the opposite direction in presence of inhibitor. Again, we can conclude that the change in $R_{ct}$ and $C_{dl}$ values is due to the gradual replacement of water molecules on the metal surface, decreasing the extent of dissolution reaction.
Figure 17 Equivalent Circuit Used in Data Fitting for the Corrosion of SS 316 in 0.5 M Sulfuric Acid in Presence of Thiophene Derivative Inhibitors
Figure 18: Nyquist Diagrams for Stainless Steel 316 in 0.5 M H$_2$SO$_4$ in Different Concentrations of 2-Thiophene Carboxylic Acid.
Figure 19. Nyquist Diagrams for Stainless Steel 316 in 0.5 M H₂SO₄ in Different Concentrations of 2-Acetyl Thiophene.
Table 7: A.C impedance data of 316 stainless steel in 0.5 M H$_2$SO$_4$ M sulfuric acid in presence and absence of 2-Thiophene carboxylic acid at -0.1 V

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$R_{ct}$ $\Omega$ cm$^{-2}$</th>
<th>$1/R_{ct}$ $\Omega^{-1}$ cm$^2$</th>
<th>$C_{dl}$ $\mu$F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>30.5</td>
<td>3.20 X 10$^{-2}$</td>
<td>62.3</td>
<td>-</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>48.4</td>
<td>2.1 X 10$^{-2}$</td>
<td>54.7</td>
<td>34.38</td>
</tr>
<tr>
<td>$1 \times 10^{-2}$</td>
<td>219.7</td>
<td>0.46 X 10$^{-3}$</td>
<td>45.0</td>
<td>85.63</td>
</tr>
</tbody>
</table>
Table 8: A.C impedance data of 316 stainless steel in 0.5 M H₂SO₄ M sulfuric acid in presence and absence of 2-Acetyl Thiophene at -0.1 V

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$R_{ct}$ Ω cm⁻²</th>
<th>$1/R_{ct}$ Ω⁻¹ cm²</th>
<th>$C_{dl}$ μF</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>52.2</td>
<td>0.0392</td>
<td>58.6</td>
<td>-</td>
</tr>
<tr>
<td>5X10⁻⁴</td>
<td>52.8</td>
<td>0.0189</td>
<td>41.3</td>
<td>51.78</td>
</tr>
<tr>
<td>1X10⁻²</td>
<td>102.4</td>
<td>0.00976</td>
<td>18.6</td>
<td>75.08</td>
</tr>
</tbody>
</table>
5- Surface Measurements

5-a Scanning Electron Microscopy

Figure 20 shows the surface features of stainless steel 316 exposed to 0.5 M H₂SO₄ with and without 2-thiophene carboxylic hydrazide for 10 minutes. Figure 20.a shows extensive corrosion in 0.5 M H₂SO₄. Figure 20.b exhibits the effect of 1.0 x 10⁻³ M 2-thiophene carboxylic hydrazide in 0.5 M H₂SO₄. The specimen surface is nearly intact as even the original polishing scratches are seen after the exposure. Few pits are visible on the specimen surface after exposure to a 0.01 M NaCl-containing 0.5 M H₂SO₄ in absence of inhibitor as shown in figure 20.b. Energy dispersive x-ray analyses (EDAX) were performed on the exposed stainless steel samples. The data are depicted in figures 21a and 21b for a sample exposed to 0.5 M H₂SO₄ and to 0.5 M H₂SO₄ + 1.0 x 10⁻³ M 2-thiophene carboxylic hydrazide, respectively. Several important observations could be noticed from the data of figure 21:

(i) The general features of the spectra are similar in both cases, where the stainless steel is only exposed to the sulfuric acid solution and that containing the inhibitor.

(ii) The amount of iron, nickel and molybdenum were affected when comparing the two graphs. Thus, the amount of iron,
nickel and molybdenum decreased in case of sample exposed to inhibitor-containing solution, whereas the amount of chromium increases.

(iii) A sulfur peak clearly appeared in the case of sample exposed to the thiophene carboxylic hydrazide sample. The decrease in the amount of iron, nickel and molybdenum and the increase in the amount of chromium indicated that the dissolution of stainless steel is inhibited. Moreover, the appearance of the sulfur peak could be attributed to the adsorption of 2-thiophene carboxylic hydrazide moiety at the stainless steel surface. This assumption was confirmed by the data obtained from surface reflectance FT-IR measurements.

5-b Surface Reflectance FT-IR

Surface reflectance FT-IR experiments were conducted on specimens that were exposed to 0.5 M H₂SO₄ and compared to stainless steel sheets exposed to 0.5 M H₂SO₄ + 1.0 x 10⁻³ M 2-thiophene carboxylic hydrazide. One important goal for this experiment is to ensure whether the inhibitor adsorbs to the surface of the metal substrate after exposure and thorough washing. Thus, figure 22 shows the data obtained by reflectance from the surface of the stainless steel (displayed in red) and that obtained from a
conventional transmission experiment of the 2-thiophene carboxylic hydrazide (displayed in blue). Region A is characterized by a strong "two-band" signal in the region 3100-3500 cm\(^{-1}\) that is characteristic of primary amines stretch [101]. Regions B and C are characteristics of the aromatic C-H stretch and bending bands of the thiophene ring at 1414 cm\(^{-1}\) and 1075 cm\(^{-1}\), respectively. A rather weak band appeared at 1660 cm\(^{-1}\) that is thought to be due to the carbonyl group in the amide linkage -C=O-NH. At this stage, we can conclude that the inhibitor is adsorbed to the surface of the substrate via the thiophene sulfur electron lone-pair, and those of the oxygen and the nitrogen atoms of the amide link. The presence of a thin oxide layer at the surface of the stainless steel is inevitable as indicated in the SEM micrographs depicted in figures 20.a and 20.b.
Figure 20a shows the surfaces of stainless steel 316 exposed to 0.5 M H₂SO₄ with and without TCH.
Figure 20.b Surface of stainless steel 316 exposed to 0.1 M H₂SO₄ and TCH in absence (a) and presence (b) of chloride ions
Figure 21. EDAX of SS 316 in 0.5 M sulfuric acid(a) and to 0.5 M sulfuric + 0.001 M 2-thiophene carboxylic hydrazide(b)
Figure 22  FT-IR Surface Reflectance Spectroscopy at SS 316 Exposed to 0.5 M Sulfuric Acid + 0.001 M 2-Thiophene Carboxylic Hydrazide (red) and Transmission Spectra of 2-Thiophene Carboxylic Hydrazide (blue)
CONCLUSIONS
Conclusions

The present work studied the corrosion behavior of stainless steel type 316 in acidic medium. The inhibitory effect and efficiencies of different thiophene derivatives were evaluated on the electrochemical behavior of stainless steel type 316 in acidic medium. The effect of adding chloride to the acid medium was also studied. The inhibitors studied showed distinct inhibition efficiencies depending on the molecular and configurational states of the inhibitor. The inhibitors appeared to be of the mixed type. This conclusion was achieved by comparing the change in the values of the anodic and cathodic Tafel slopes. Inhibition efficiencies of ca. 97% were realized using these inhibitors in 0.5 M \( \text{H}_2\text{SO}_4 \). The presence of chloride ions in the acid medium was found to be detrimental and initiated pitting to the surface of the alloy. The application of thiophene carboxylic hydrazide hindered the formation of pits on the surface of stainless steel. Increasing the concentration of the inhibitor caused a gradual decrease in the rate of corrosion. Opposite effect was observed on rate of corrosion by increasing the concentration of \( \text{H}_2\text{SO}_4 \). The order of increasing the percentage of inhibition efficiency was 2-thiophene carboxylic hydrazide > 2-Thiophene carboxylic acid > 3-thiophene carbaldhyde > 2-acetyl thiophene. This sequence was explained in terms of the order of stability.
of the thiophene derivatives in solution and consequently their tendency to adsorb at the stainless steel surface, the position of the substitution on the ring, and the number and nature of substituent. On the other hand, increasing the temperature resulted in a decrease in the inhibition efficiencies. Heat of adsorption was calculated as \(-38.625\) kJ.mol\(^{-1}\) for thiophene carboxaldehyde. The negative values calculated for \(\Delta H^o\) indicates that the adsorption process is exothermic. Moreover, the magnitudes of \(\Delta S^o\) and \(\Delta G^o\) indicate that a replacement process took place during the adsorption of the inhibitor molecules at the surface of the stainless steel.

Surface measurements indicated that the surface of the stainless steel is protected in presence of the inhibitor in aggressive medium. Also, surface reflectance FT-IR indicated that the inhibitor adsorbs effectively at the surface of stainless steel.
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-thiophene carboxylic hydrazide > \( \text{2-thiophene carboxylic acid} \) > \( \text{2-thiophene carboxaldehyde} \) > \( \text{2-acetyl thiophene} \)

It is followed by a description of the experimental setup and the results, which show a clear hierarchy of the reactivity of the thioether compounds. The authors observe a significant difference in the reactivity pattern, which is attributed to the presence of the thioether moiety.

The results indicate that the reaction rates decrease in the order of hydrazide, acid, aldehyde, and finally acetyl thiophene, which is consistent with the electronic properties of the compounds. The authors also discuss the implications of these findings for the design of new materials and pharmaceuticals.
يدخل الفولاذ في صناعة السيارات والصناعة الإلكترونية وتطبيقات أخرى. ويعتبر عنصري الحديد والكروم من المكونات الرئيسية الداخلة في تكوينه إذ تتراوح نسبتهما بين 60-75% و 10-25% لكل منهما على التوالي كما يوجد بعض العناصر الأخرى بنسبة مختلفة كالنيكل، الكوبالت، الموليبدينيوم، المنغنيز والكربون. أحد أهداف هذا الرسالة هو استخدام قياسات كهروكيميائية وسطحية لدراسة سلوك الفولاذ من نوع 316 (نسبة العناصر الداخلة في تركيبه موجودة في جدول (1)) في الوسط الحمضي في وجود و عدم وجود مشتقات مختلفة لمركب الثايوفيدين. كما توجد أهداف أخرى كدراسة تأثير أيون الكلورايد في الوسط الحمضي على سلوك تآكل الفولاذ وحساب كفاءة المثبتات المستخدمة وتحديد المعامل الحراري وطبيعة الامتصاز لهذه المثبتات على سطح الفولاذ.

تم استخدام طرق كهروكيميائية مختلفة كطريقة تغير الجهد مع الزمن (البوتشوشيمايكا)، وطريقة تآكل ومقاومة الاستقطاب لترقيم تأثير المثبتات على تآكل الفولاذ 316.

كما تم استخدام تحاليل سطحية لمعرفة شكل والتركيب الكيميائي للسطح كجهاز الميكروسكوب الإلكتروني للمسح السطحي، وطريقة القياس السطحي الانعكاسي باستخدام الأشعة تحت الحمراء وطريقة القياس التشتيتي باستخدام أشعة أكس.\n
لجهزة الإشراف على الأطروحة

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تقييم أداء بعض المثبطات العضوية لتآكل الفولاذ
غير القابل للصدأ باستخدام طرق كهروكيميائية وسطحية مختلفة

أطروحة مقدمة إلى
عمادة الدراسات العليا
جامعة الإمارات العربية المتحدة

مریم حسن سعید الحسن

لمتطلبات الحصول على درجة الماجستير

في
علوم وهندسة المواد

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