Inhibitive effect of thiosemicarbazone derivative on corrosion of mild steel in hydrochloric acid solution

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Abstract

Inhibition effect of 3-pyridinecarboxaldehyde thiosemicarbazone (META) on the mild steel corrosion in one molar hydrochloric acid was investigated using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Results showed that (META) is an effective inhibitor for mild steel corrosion in 1.0 M HCl solutions and inhibition efficiency is >94% at inhibitor concentration of 0.01 M. Adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm. The thermodynamic values indicated that adsorption of 3-pyridinecarboxaldehyde molecule is a spontaneous process and it adsorbs chemically as well as physically. Polarization studies showed that 3-pyridinecarboxaldehyde is a mixed-type inhibitor. Scanning electron microscope (SEM) micrographs revealed that inhibition occurs due to adsorption of 3-pyridinecarboxaldehyde molecules at metal/solution interface.

Keywords: Acid corrosion inhibition; EIS; SEM; Adsorption

1. Introduction

Evaluation of corrosion inhibitors for mild steel in acidic media is important for some industrial facilities. Acid solutions are generally used for the removal of rust and scale in industrial processes. Hydrochloric acid is widely used in the pickling, cleaning and descaling of steel and ferrous alloys [1]. Most of the effective corrosion inhibitors are organic compounds containing nitrogen, oxygen, sulphur, aromatic rings and π-electrons in their structures [2, 3]. The effectiveness of theses organic compounds as corrosion inhibitors has been interpreted in terms of their molecular structure, molecular size, molecular mass, presence of hetero-atoms and adsorptive tendencies [4]. The first stage in the action mechanism of these compounds in acid media is their adsorption on the metal surface [5]. The various inhibition mechanisms are considered regarding different situations created by changing various factors such as medium and inhibitor in the system metal/acid /inhibitor [6].

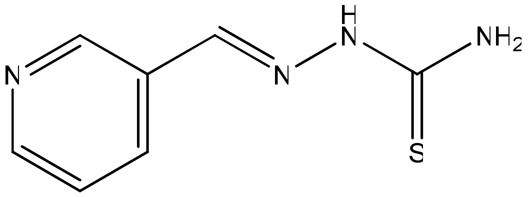
Large numbers of organic compounds were studied to investigate their corrosion inhibition potential. For example, the effect of organic nitrogen compounds on the corrosion behaviour of iron and steel in acidic solutions are usually employed for their rapid action [7-10]. The existing data show that most of the organic inhibitors act by adsorption on the metal surface. The adsorption of inhibitors takes place through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, multiple bonds or aromatic rings. The inhibition efficiency should increase in the order O < N < S < P [11]. Nitrogen-containing heterocyclic compounds are considered to be effective corrosion inhibitors.

The primary step in the action of organic corrosion inhibitors in acid solutions is usually adsorption at the metal–solution interface. The adsorption process depends on the electronic characteristic of the molecules (adsorbate), the chemical composition of the solution, nature of the metal surface, temperature of the reaction and on the electrochemical potential at the metal–solution interface [7-9]. The adsorption requires the existence of attractive forces between the adsorbate and the metal. According to the type of forces, adsorption can be physisorption or chemisorption or a combination of both [10,11].

In continuation of the work on the development of new organic compounds as corrosion inhibitors [12-15], present work describes the investigation of inhibitive action of (META) on corrosion of the mild steel in one molar hydrochloric acid solutions using weight loss, potentiodynamic polarization , electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The choice of this compound was based on molecular structure considerations. The (META) molecule is made up of a pyridine ring of planar structure with delocalized pi electrons (aromaticity), a thisemicarbazone moiety. These structural features favour the interaction of 3-pyridinecarboxaldehyde (META) with mild steel surface. The IUPAC name and structure of 3-pyridinecarboxaldehyde (META) is given in the experimental part.

2. Experimental details

3-pyridinecarboxaldehyde (META) was analytical grade. The molecular structure is shown below:



Chemical structure of 3-pyridinecarboxaldehyde .

The aggressive solution (1.0 M HCl) was prepared by dilution of analytical grade 37 % HCl solution with double-distilled water. Prior to all measurements, the steel samples with the following composition (0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron) were abraded with different emery paper up to 4/0 grit size, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and drying at room temperature.

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (2.5 cm × 2 cm × 0.05 cm). The immersion time for the weight loss was 6 h at 30 ± 1 °C . After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Triplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in mg cm^{-2} h^{-1}.

The electrochemical measurements were performed in a typical three-compartment glass cell consisted of the mild steel specimen as working electrode (WE), platinum counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode. The counter electrode was separated from the working electrode compartment by fritted glass. The reference electrode was connected to a Luggin capillary to minimize IR drop. Solutions were prepared from bidistilled water of resistivity 13 MΩ cm, the mild steel electrode was abraded with different grit emery papers up to 4/0 grade, cleaned with acetone, washed with bidistilled water and finally dried.

The electrode potential was allowed to stabilize 60 min before starting the measurements. All experiments were conducted at 30 ± 1 °C.

Measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry Framework system based on the ESA400, Gamry applications that include dc105 for dc corrosion measurements, EIS300 for electrochemical impedance spectroscopy measurements along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.

Tafel polarization curves were obtained by changing the electrode potential automatically from (-750 to -280 mV_{SCE}) at open circuit potential with scan rate of 1.0 mV s^{-1}. Impedance measurements were carried out in frequency range from 10 kHz to 1.0 mHz with an amplitude of 10 mV peak-to-peak using ac signals at open circuit potential.

The values of inhibition efficiency from charge transfer resistance and corrosion current density were calculated using equations (1) and (2), respectively:

$$IE_{\mathrm{p}}(\%) = \frac{j^{\mathrm{o}}_{\mathrm{corr}} - j_{\mathrm{corr}}}{j^{\mathrm{o}}_{\mathrm{corr}}} \times 100 \qquad (1)$$

where $j^{\mathrm{o}}_{\mathrm{corr}}$ and j_{corr} are corrosion current densities obtained in the absence and presence of inhibitor, respectively.

$$\tau_{\mathrm{EIS}}\% = \frac{R_{\mathrm{ct}} - R^{\mathrm{o}}_{\mathrm{ct}}}{R_{\mathrm{ct}}} \times 100 \qquad (2)$$

where R_{ct} and $R^{\mathrm{o}}_{\mathrm{ct}}$ are charge transfer resistances in the presence and absence of inhibitor, respectively; and Scanning electron microscopy (SEM) was used to study the surface morphology of the mild steel. The mild steel specimens of size 2.5 cm × 2.0 cm × 0.025 cm were immersed for 3 h in 1.0 M HCl solution containing 0.01 M (MATE).

3. Results and discussion

3.1. Weight loss tests

Gravimetric measurements of steel were investigated in 1.0 M HCl in the absence and presence of various (META) concentrations at 6 h of immersion and at 30 ± 1 °C. The inhibition efficiency ($\alpha\%$) was calculated by the following relation:

$$\sigma_{\mathrm{W}}\% = \frac{\mathrm{W_{corr}} - \mathrm{W_{corr\,(inh)}}}{\mathrm{W_{corr}}} \times 100 \qquad (1)$$

where $\mathrm{W_{corr}}$ and $\mathrm{W_{corr\,(inh)}}$ are the corrosion rates of steel in the absence and presence of the organic compound, respectively.

Table 1 collects the corrosion rates and Fig. 1 shows the variation of inhibition efficiencies evaluated from weight loss measurements for different inhibitor concentrations in 1.0 M HCl. The corrosion rate decreases with (META) concentration and in turn the inhibition efficiency ($\sigma_{\mathrm{W}}\%$) increases to attain 95 %. From weight loss measurements, we can conclude that (META) is an excellent inhibitor.

Table 1

Inhibition efficiency $\sigma_{\mathrm{W}}\%$ data obtained from weight loss measurements for mild steel in 1.0 M HCl solutions in absence and presence of various concentrations of META at 30 ± 1 °C

[Inhib] / M	Corrosion rate / mg cm^{-2} h^{-1}	$\sigma_{\mathrm{W}}\%$
Blank	**1.05**	**---**
10^{-5}	0.25	75
10^{-4}	0.18	82
10^{-3}	0.11	89
10^{-2}	0.05	95

The effect of temperature on the inhibition performance of (META) for mild steel in one molar hydrochloric acid solution in the absence and presence of 0.01 M at temperature ranging from 30 to 60 °C was obtained by weight loss measurements. The results were given in Fig. 2. This figure shows that inhibition efficiency decreases with increasing the solution temperature from 30 to 60 °C. This can be attributed to increased rate of desorption of inhibitor molecules from the surface of mild steel with increasing temperature. These results confirmed that (META) acts as a good inhibitor for mild steel in one molar hydrochloric acid solution in the range of temperature studied.

In order to have better understanding of thermodynamic properties of the mild steel corrosion processes in the presence of (META), a detailed study on corrosion behaviour of mild steel was carried out at a temperature range 30 to 60 °C using weight loss technique. The corrosion reaction can be regarded as an Arrhenius-type process, the rate of which is given by:

$$C_{\mathrm{R}} = \lambda \exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \quad (3)$$

where E_a is the apparent activation energy for corrosion of the mild steel in 1.0 M HCl solution, R the general gas constant, λ the Arrhenius pre-exponential factor and T the absolute temperature. A plot of the logarithm of the corrosion rate ($\mathrm{mg\ cm^{-2}\ h^{-1}}$) of mild steel obtained from weight loss measurements vs. 1 / T gave a straight line as shown in Fig. 3a. The values of E_a and λ obtained from the slope and intercept, respectively of this line (Fig. 3a) were presented in Table 2.

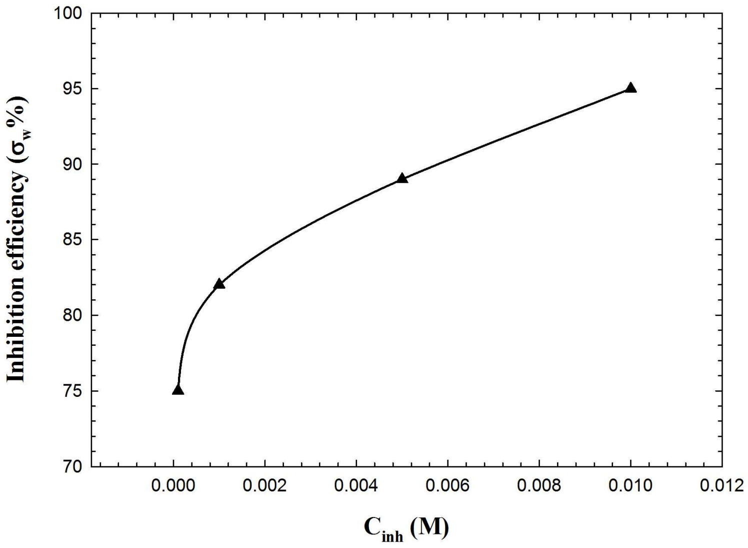


Fig. 1: Variation of inhibition efficiency (σ_W%) with the concentration of META for mild steel in 1.0 M HCl.

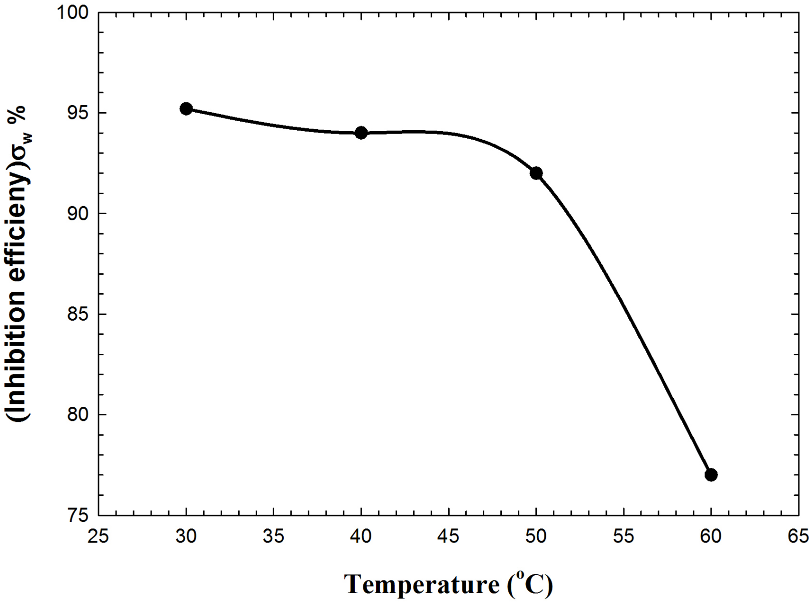
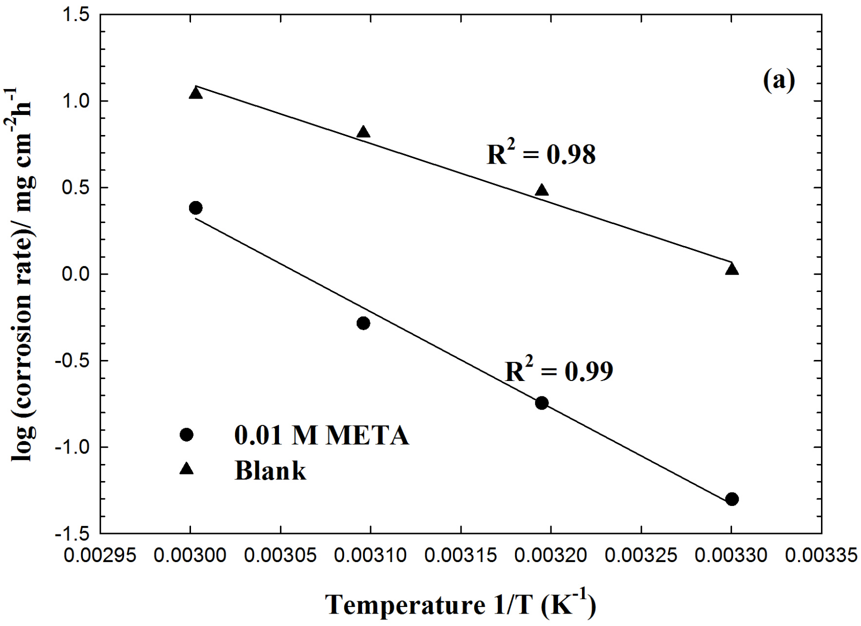


Fig. 2: Effect of temperature on σ_W% for the mild steel in 1.0 M HCl in the presence of 0.01 M META.



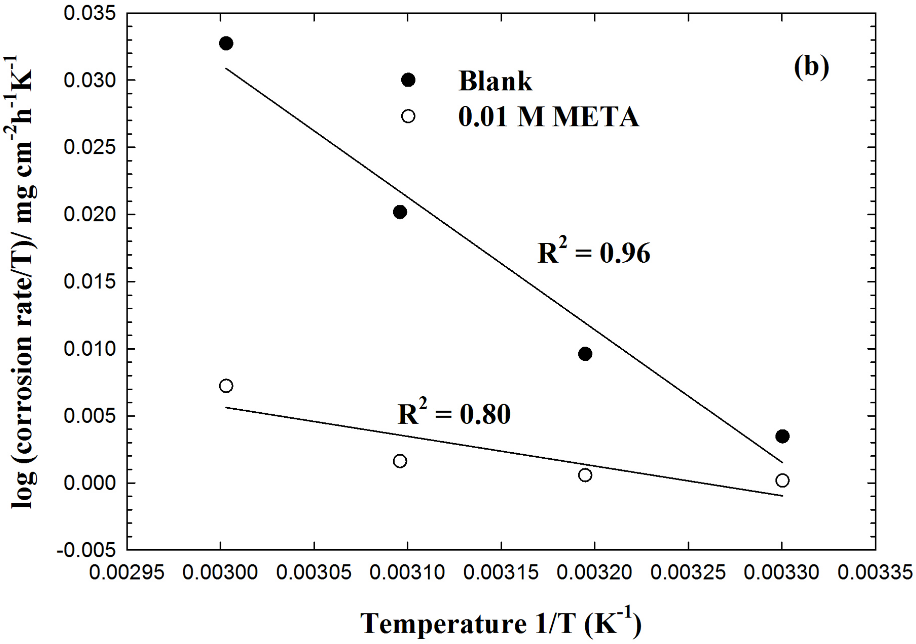


Fig. 3: Arrhenius plots of: **(a)** log corrosion rate vs. 1 / T; **(b)** log (*corrosion rate* / T) vs. 1 / T for the mild steel in 1.0 M HCl solution in the absence and presence of 0.01 M META.

An alternative formula of the Arrhenius equation is the transition state equation:

$$C_{\mathrm{R}} = \frac{RT}{Nh}\exp\left(-\frac{\Delta H^*}{RT}\right)\exp\left(\frac{\Delta S^*}{R}\right) \quad (4)$$

where N is the Avogadro's number, h the Planck's constant, ΔH^* the enthalpy of activation and ΔS^* the entropy of activation. Fig. 3b showed a plot of log (C_{R} / T) versus 1 / T giving a straight line with a slope of ($-\Delta H^*$ / 2.303 R) and an intercept of log (R / Nh + ΔS^* / 2.303 R) from which the values of ΔH^* and ΔS^* were calculated and given in Table 2. The data in Table 2 reveal that the values of thermodynamic activation functions (E_a and ΔH^*) for corrosion of the mild steel in 1.0 M HCl solution in the presence of the inhibitor are higher than those in the free acid solution. Higher values of E_a and ΔH^* in the presence of inhibitor indicate more energy is required for dissolution of the mild steel in 1.0 M HCl in presence of (META). Similar results were reported by other authors [16]. The increase in apparent activation energy for the mild steel dissolution in inhibited solution may be interpreted as physical adsorption that occurs in the first stage [17]. Szauer and Brand explained [18] that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature.

The pre-exponential factor λ in the Arrhenius equation (Eq. 3) for corrosion process, heterogeneous reactions, is related to the number of active centers. These active centers have different energy if energetic surface heterogeneity is assumed. In present case $E_{a,inh} > E_{a,HCl}$ that is the inhibitor is adsorbed on the most active adsorption sites (having the lowest energy) and corrosion process occurred predominantly on the active sites of higher energy. Values of E_a and λ obtained in the presence of META are higher than those obtained in free acid solutions which mean that the presence of META results in high number of active centres remain uncovered with the inhibitor.

Table 2 Activation parameters Ea, ΔH^* and ΔS^* for the mild steel dissolution in 1.0 M HCl in the absence and the presence of 0.2 M (META)

	E_a (kJmol^{-1})	**λ**	**ΔH^* (kJmol^{-1})**	**ΔS^* (J K^{-1} mol^{-1})**
Blank	**-65.617**	**2.39 ×10^{11}**	**18.9**	**-196.3**
0.2M META	**-106.25**	**9.5 ×10^{16}**	**42.3**	**-182.2**

Inspection of Table 2 showed that value of enthalpy of activation is positive and higher in the presence of inhibitor. The positive sign of ΔH^* reflects the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow in the presence of inhibitor. The entropy of activation ΔS^* is higher (-182 J K^{-1} mol^{-1}) in the presence of inhibitor than that (-191 J K^{-1} mol^{-1}) in the absence of inhibitor. This is what would be expected, since adsorption of inhibitor is an exothermic process and is always accompanied by a decrease of ΔS^*[19]. The reason could be explained as follows [12,19]: adsorption of organic inhibitor molecules from the aqueous solution is regarded as a quasi-substitution process between the organic compound in the aqueous phase [$Org_{(sol)}$] and water molecules at the electrode surface [$H_2O_{(ads)}$]. In this situation, the adsorption of organic inhibitor is accompanied by desorption of water molecules from the surface. Thus, while the adsorption process for the inhibitor is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. The thermodynamic values obtained are the algebraic sum of the adsorption of organic molecules and desorption of water molecules [19]. Therefore, the gain in entropy is attributed to the increase in solvent entropy. The positive values of ΔS^* also suggest that an increasing in disordering takes place in going form reactants to the metal/solution interface [9], which is the driving force for the adsorption of inhibitors onto the mild steel surface.

Compared to chemical methods, electrochemical techniques can obtain the instantaneous corrosion rate, implement in-situ measurement, and provide plenty of information. Thus, they are expected to be applied to detect and monitor corrosion of metals and alloys in various corrosive media. Several electrochemical techniques are available to determine corrosion rate, such as the potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

3.2. Potentiodynamic polarization measurments

Figure 4 shows the cathodic and anodic polarization curves recorded for mild steel in aerated stagnant 1.0 M HCl solutions without and with various concentrations of (META) at a scan rate of 1.0 mV s^{-1} at 30 °C. It is obvious, in all cases, that both the anodic and cathodic branches of the polarization curves display Tafel behaviour. The values of the corrosion current density (j_{corr}) for mild steel corrosion reaction without and with inhibitor were determined, therefore by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential (E_{corr}). Table 3 represents the influence of (META) on the corrosion parameters of mild steel electrode in aerated stagnant 1.0 M HCl solutions at 30 °C.

As it can be seen from Fig. 4, in all cases, the anodic and cathodic reactions are affected by (META). The cathodic as well as the anodic reactions are markedly affected by the inhibitor toward lower current densities. Based on that there is no definite shift in the corrosion potential and the marked decrease of the current density upon introducing (META) in the aggressive solution, META is considered as mixed-type inhibitor. These observations demonstrate that the addition of (META) reduces mainly the cathodic process and also retards the anodic process. The corrosion current desnity (j_{corr}) decreased when the concentration of (META) was increased. This indicates the inhibiting effect of (META) on the acid corrosion of mild steel.

Following the electrochemical kinetic laws, the rates of the anodic and cathodic reactions in acidic solutions, in presence of an adsorbed inhibitor on the metal surface, can be described by:

$$i_a = k_a\,(1-\theta)\,\exp\,[Fz\beta\,(E - \psi_1) / RT] \qquad (5)$$

$$i_c = k_c\,[H_3O^+]\,(1-\theta)\,\exp\,\{-F[\alpha E + (1-\alpha)\,\psi_1] / RT\} \qquad (6)$$

where k_a and k_c are the corresponding rate constants, θ is the fraction of the electrode surface covered by the inhibitor, E is the electrode potential relative to solution, ψ_1 is the potential drop in the outer part of the double layer, α and β are the symmetry factors of both reactions, while z is the charge of the metal ions in the solution.

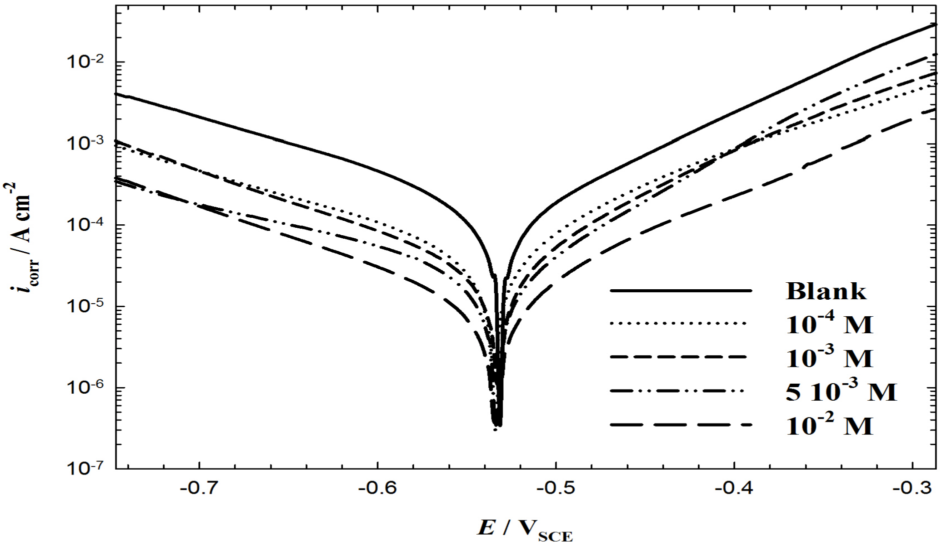


Fig. 4: Potentiodynamic polarization curves for the corrosion of mild steel in 1.0 M HCl in the absence and presence of different concentrations of META at 30 ± 1 °C.

It is assumed that hydrogen ionization as well as the proceeding of electrochemical reactions can be neglected on the surface sites covered by the inhibitor. The studied inhibitors affect the rate of the corrosion process mainly through the variation of the degree of surface coverage (θ), i.e., by blocking effect they exert. The adsorption of the inhibitor cations in OHL leads to a decrease of ψ_1 i.e., to its shift to more positive values. This in turn results in a decrease of the concentration of the hydrogen ions in the surface layer and a corresponding increase of the overpotential of hydrogen evolution.

Table 3 Electrochemical kinetic parameters, protection efficiencies ($IE_p(\%)$) and rates of corrosion associated with potentiodynamic polarization measurements recorded for mild steel in 1.0 M HCl solutions in absence and presence of various concentrations of META at 30 ± 1 °C.

[Inhib] / M	**β_a / mV dec^{-1}**	**β_c / mV dec^{-1}**	**-E_{corr} / mV(SCE)**	**(j_{corr}) / µA cm^{-2}**	$IE_p(\%)$	**Corrosion rate /mpy**
Blank	**107**	**147**	**531**	**149**	**---**	**68.24**
10^{-4}	**120**	**180**	**535**	**57**	62	26.26
10^{-3}	**100**	**160**	**533**	**35**	77	15.86
5 10^{-3}	**98.2**	**186**	**535**	**25**	83	11.34
10^{-2}	**105**	**149**	**534**	**12**	92	5.38

The shapes of the polarization plots, in all cases, for inhibitor-HCl containing solutions are not substantially different from those of inhibitor-free HCl solutions. The presence of these inhibitors decreases the corrosion rate but does not change other aspects of the behaviour. This means that the inhibitors do not alter the electrochemical reactions responsible for corrosion. In addition, the absence of significant changes in the cathodic and anodic Tafel slopes in the presence of (META) as indicated in Table 3, indicates that the hydrogen evolution as well as anodic metal dissolution reactions are slowed down by the surface blocking effect of the inhibitor, as previously mentioned.

The results obtained from potentiodynamic polarization measurements for the mild steel in one molar hydrochloric acid solution in the absence and presence of different concentrations of (META) were presented in Fig. 4. It can be seen that both the cathodic and anodic reactions were suppressed in the presence of (META), which suggested that (META) reduced both the anodic dissolution and the cathodic hydrogen evolution reactions.

From Table 3, it is clear that the values of both anodic and cathodic Tafel slope constants were more or less constant suggesting that presence of (META) molecules does not alter the mechanism of corrosion in HCl environment.

3.3. Electrochemical impedance spectroscopy (EIS) studies

Results obtained from EIS measurements for mild steel in 1.0 M HCl solution in the absence and presence of different concentrations of (META) were presented in the form of Nyquist (Fig. 5) plots. The plots showed a depressed capacitive loop which arises from the time constant of the electrical double layer and charge transfer resistance. The impedance of the inhibited mild steel increases with increase in the inhibitor concentration and consequently the inhibition efficiency increased. A depressed semicircle is mostly referred to as frequency dispersion which could be attributed to different physical phenomena such as roughness and inhomogeneities of the solid surfaces, impurities, grain boundaries and distribution of the surface active sites [20]. Inhibitor molecules get adsorbed on the mild steel/acid solution interface and thereby produce a barrier for the metal to diffuse out to the bulk and this barrier increases with increasing the inhibitor concentration [21].

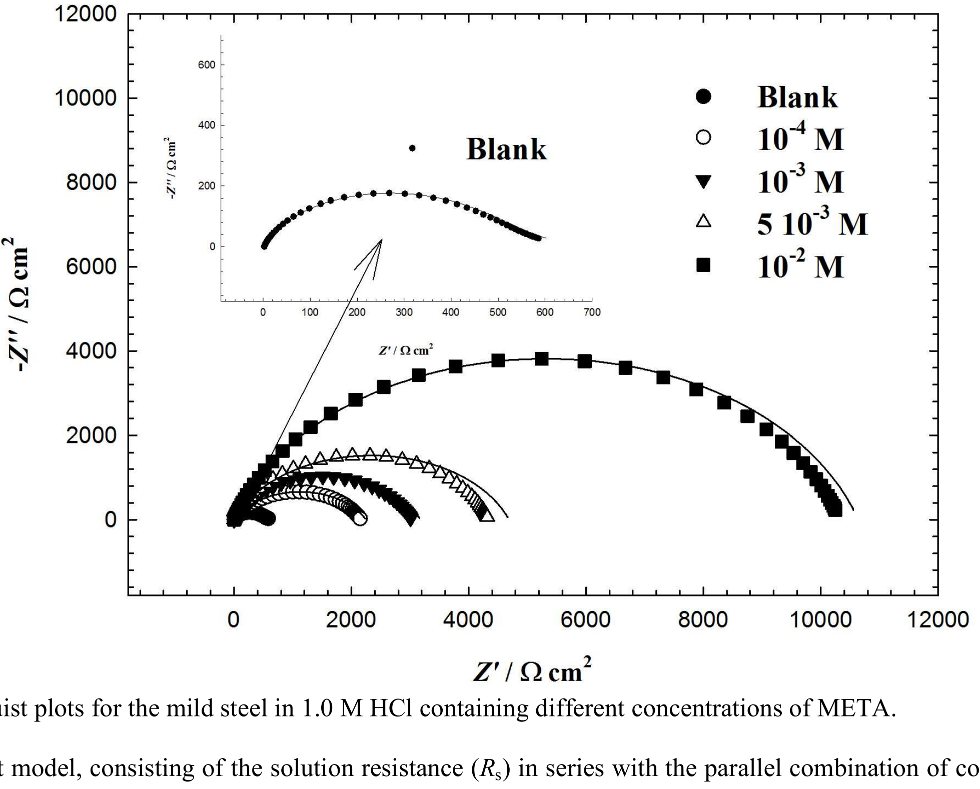


Fig. 5: Nyquist plots for the mild steel in 1.0 M HCl containing different concentrations of META.

The simplest model, consisting of the solution resistance (R_s) in series with the parallel combination of constant phase element (CPE) in place of double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}), was used to evaluate the experimental EIS results. This equivalent circuit was presented in Fig. 5 and was used previously to model the mild steel/acid solution interface [22]. The charge transfer resistance (R_t) must be corresponding to the resistance between the metal and OHP (outer Helmholtz plane) and can be calculated from the difference in impedance at lower and higher frequencies [23].

Mathematically, amplitude of CPE is given by the relation:

$$Z_{\mathrm{CPE}} = Q^{-1}(j\omega)^{-1} \quad (7)$$

where Q is the magnitude of the CPE, j is the imaginary unit, ω is the angular frequency ($\omega = 2\pi f$, the frequency in Hz), and n is the phase shift which gives details about the degree of surface inhomogeneity. When $n = 1$, this is the same equation as that for the impedance of a capacitor, where $Q = C_{\mathrm{dl}}$.

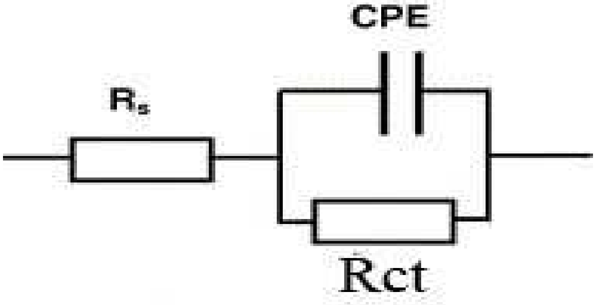


Fig. 6: The electrochemical equivalent circuit used to fit the impedance results.

Table 4 Electrochemical parameters calculated from EIS measurements for mild steel in 1.0 M HCl solutions in absence and presence of various concentrations of META at 30 ± 1 °C.

[Inhib] / M	R_s/ Ω cm^2	R_{ct}/ Ω cm^2	CPE $\mu\Omega^{-1}\mathrm{cm}^{-2}\mathrm{S}^{n_1}$	n	τ_{EIS}%
Blank	1.2	599	210	0.73	---
10^{-4}	1.2	2162	15	0.70	72.3
10^{-3}	0.9	3025	12	0.76	80.2
$5\ 10^{-3}$	0.85	4340	10	0.79	86.2
10^{-2}	1.4	10327	7	0.81	94.2

Various electrochemical impedance parameters obtained by fitting the Nyquist plots were listed in Table 4. It is clear that addition of (META) into the corrosive solution caused an increase in the charge transfer resistance (R_{ct}) and a decrease in the double layer capacitance (C_{dl}) which can be given as [24]:

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

where ε_0 is the vacuum dielectric constant, ε is the local dielectric constant, d is the thickness of the double layer, and A is the surface area of the electrode. It is obvious that a decrease in C_{dl} can happen if the inhibitor molecules (low dielectric constant) replace the adsorbed water molecules (high dielectric constant) on the mild steel surface. The capacitance is inversely proportional to the thickness of the double layer. Thus, decrease in the C_{dl} values could be attributed to the adsorption of (META) on the metal surface. Decrease in the capacitance, which can result from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, strongly suggests that the inhibitor molecules adsorbed at the metal/solution interface. In the absence and in the presence of inhibitor, phase shift value remained more or less identical; this indicates that the charge transfer process controls the dissolution mechanism [25] of mild steel in one molar hydrochloric acid solution in the absence and in the presence of (META.

3.4. Adsorption isotherm

Adsorption of organic inhibitor molecules is often a displacement reaction involving removal of adsorbed water molecules from the metal surface:

$$\mathrm{Org}_{(\mathrm{sol})} + \mathrm{xH_2O}_{(\mathrm{ads})} \rightarrow \mathrm{Org}_{(\mathrm{ads})} + \mathrm{xH_2O}_{(\mathrm{sol})} \quad (9)$$

where x is the size ratio, that is, the number of water molecules replaced by one organic inhibitor molecule. In order to understand the mechanism of corrosion inhibition, adsorption behavior of the organic compounds at mild steel/acid solution interface must be known. Basic information dealing with interaction between inhibitor molecules and the metal surface can be provided by adsorption isotherms.

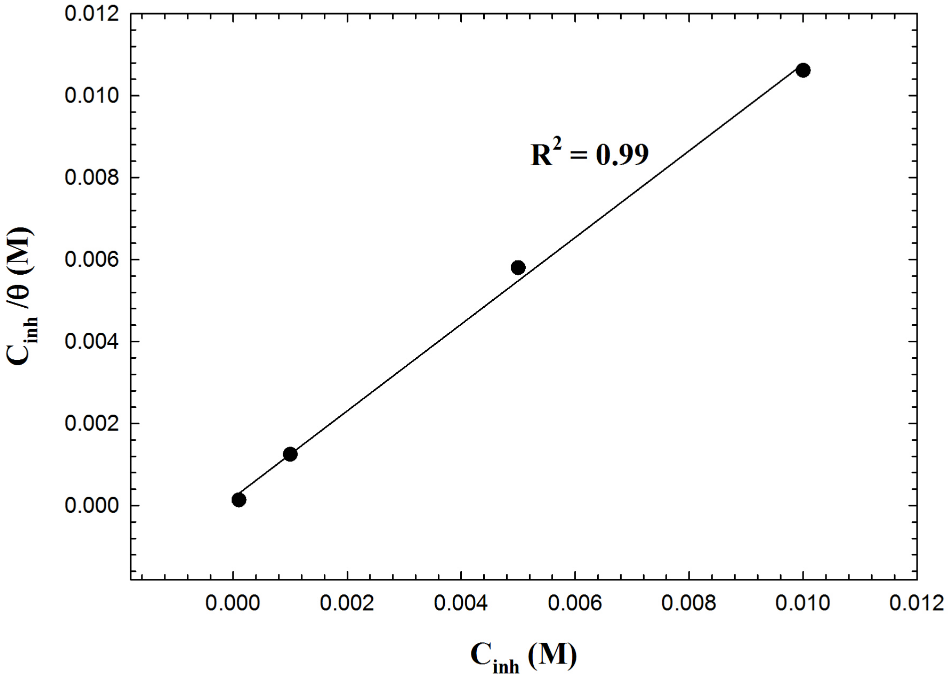


Fig. 7: Langmuir adsorption isotherm plots for the adsorption of the META on the mild steel surface in 1.0 M HCl solution at 30 ± 1 °C.

The values of degree of surface coverage (θ) for the inhibitor were obtained from weight loss, potentiodynamic and EIS data. The data obtained from these techniques have been tested with several adsorption isotherms (such as Frumkin, Langmuir, Temkin, Freundlich, Bockris–Swinkels and Flory–Huggins isotherms). The Langmuir adsorption isotherm was found to provide the best description of the adsorption behavior of (META) at the mild steel/acid solutions interface. The plot of C_{inh} / θ versus C_{inh} yields straight lines (Fig. 7) with regression coefficients (R^2) almost equal to 1. This suggested that (META) in present study obeyed the Langmuir adsorption isotherm model which is given as:

$$\frac{C_{inh}}{\theta}=\frac{1}{K_{ads}}+C_{inh} \tag{10}$$

where C_{inh} is the molar concentration of inhibitor and K_{ads} is the equilibrium constant for the adsorption/desorption process.

3.4. Scanning electron microscopic (SEM) study

The SEM micrographs were presented in Fig. 8 to study the morphology of the metal surface in absence and presence of META.The micrographs showed properties of the mild steel surface after immersion in 1.0 M HCl in the absence and the presence of 0.01 M (META) at 30 °C. The mirographs revealed that the steel surface in presence of META improved while the steel surface immersed in one molar hydrochloric acid solution was rough and covered with corrosion products. These indicated that (META) decrease the corrosion rate of steel in hydrochloric acid by forming a protective film on the steel surface and thereby reduce the steel corrosion rate.

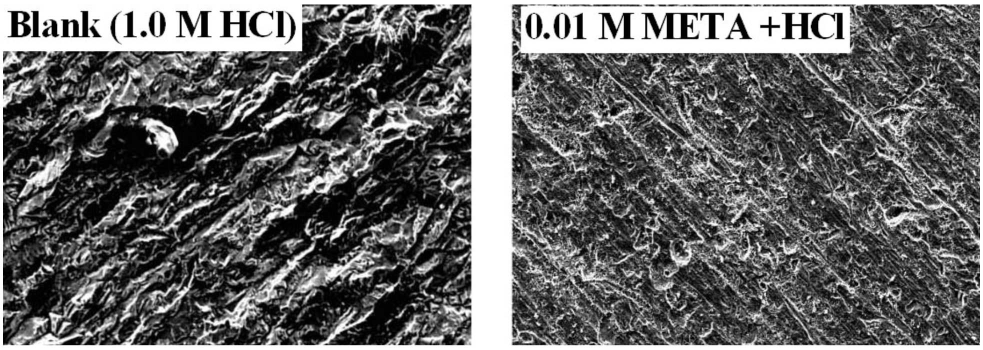


Fig. 8: SEM micrographs of the surface of the mild steel specimens after immersion in 1.0 M HCl: (a) without META [1]; (b) containing 0.01 M META.

3.5. Mechanism of corrosion inhibition

In general, the phenomenon of adsorption is influenced by the nature and surface charge of the metal and by the chemical structure of inhibitors. The surface charge of the metal is due to the electrical field which emerges at the interface on immersion in the electrolyte. It can be determined according to Antropov [26] by comparing the potential of zero charge (PZC) and the stationary potential of the metal in the electrolytic medium. As PZC corresponds to a state at which the surface is free from charges, at the stationary (corrosion) potential the metal surface will be positively or negatively charged. Hence, it is necessary to have reliable data about PZC.

It is well known that the steel surface is positively charged in HCl solutions at the free corrosion potential. Based on this observation, the mechanism of adsorption of (META) on iron surface in HCl solutions is quite clear. Cl^- ions first adsorbed at the electrode/solution interface at the corrosion potential through electrostatic attraction force due to the excess positive charge at this interface. This process changes the charge of the solution side of the interface from positive to negative, and thus facilitating physical adsorption of (META) cations. Thus, cations of (META) are able to electrostatically adsorb on the electrode surface covered with primary adsorbed Cl^- ions, therefore that Cl^- ions promote the physical adsorption of (META) cations on the electrode surface.

In addition to the physical adsorption, there should be chemical adsorption owing to the coordinate bonds that may be formed between the lone electron pairs of the unprotonated 3-pyridinecarboxaldehyde thiosemicarbazone (META) and the vacant d-orbital in the iron surface to form a coordinate type of a bond which enhanced the combination intension between the inhibitor molecule and electrode surface, On the other hand, the resultant cationic species can be adsorbed directly on cathodic sites and retard the rate of the hydrogen evolution reaction. This is responsible for the observed cathodic inhibiting effect of the (META).

Literature survey shows that few investigations have shown that adsorption could also occur through hydrogen bonding [27,28].

Adsorption in this case is assisted by hydrogen bond formation between thiosemicarbazone derivative and oxidized surface species. This type of adsorption should be more prevalent for protonated N-atom, because the positive charge on N-atom is conductive to the formation of hydrogen bonds. Unprotonated N-atom may adsorb by direct chemisorption or by hydrogen bonding to a surface oxidized species. The extent of adsorption by the respective modes depends on the nature of the metal surface. Adsorption by direct chemisorption, for unprotonated N-atom, on an exposed metal atom is more probable in the active region. In this region, although the unprotonated N-atom can interact with oxidized metal and the corrosion intermediates by hydrogen bonding, little is contributed to corrosion inhibition because corrosion intermediates and surface oxides could not form a stable compact layer on the metal surface. Effective inhibition is predominantly provided by the direct coordination of unprotonated N-atom to metal atoms. In the passive region where the metal surface is covered by an adherent oxide protective layer, the direct coordination of nitrogen to an exposed metal atom is a remote event. Protonated and unprotonated N-atoms are adsorbed onto metal through hydrogen bond formation. These results confirm the importance of hydrogen bonding in effective corrosion inhibition in the passive region.

4. Conclusion

The following are the main conclusions that can be drawn are:

1. The selected thiosemicarbzone derivative was found to be effective inhibitor for mild steel corrosion in 1.0 M HCl solutions.
2. Tafel polarization studies have shown that the selected compound suppresses both anodic and cathodic process and thus acts as mixed-type inhibitor.
3. In determining the corrosion rates, electrochemical studies gave similar results.
4. The results of impedance indicate that the value of both polarization resistance and inhibition efficiency tend to increase by increasing the inhibitor concentration. This result can be attributed to increase of the thickness and integrity of the adsorbed thiosemicarbazone derivative (META).

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