Electrochemical behavior of nickel in nitric acid and its corrosion inhibition using some thiosemicarbazone derivatives

K.F. Khaled

**Abstract**

The adsorption and corrosion inhibition behavior of three selected thiosemicarbazone derivatives, namely 3-pyridinecarboxaldehyde thiosemicarbazone (META), isonicotinaldehyde thiosemicarbazone (PARA) and 2-pyridinecarboxaldehyde thiosemicarbazone (ORTHO) at the nickel surface were studied electrochemically by Tafel and impedance methods and computationally by carrying out Monte Carlo searches of configurational space on nickel/thiosemicarbazone derivative system. Electrochemical measurements showed that the inhibition efficiency of these compounds increased with increase in their concentration. The recorded inhibition efficiencies of the three tested thiosemicarbazone increase in the order: META > PARA > ORTHO. Polarization studies showed that these compounds act as mixed-type inhibitors for nickel corrosion in 1.0 M HNO₃ solutions. Results obtained from Tafel and impedance methods are in good agreement. Thiosemicarbazone derivatives have been simulated as adsorbate on Ni (1 1 1) substrate and the adsorption energy, binding energy and the low energy adsorption sites have been identified on nickel surface.

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**1. Introduction**

The anodic behavior and the mechanism of passivation of nickel and the properties of passive nickel have been studied extensively; perhaps more widely than any other element, except, possibly, iron. Despite this, there is by no means agreement either on the mechanism of passivation of nickel or on the composition and thickness of the passive layer [1]. In acidic solutions: nickel is capable of passivating to a considerable extent. This is a feature not predicted by the potential-pH equilibrium diagram and is one reason why in practice the corrosion resistance of nickel in acid solutions is better than that predicted from considerations of thermodynamic equilibria. Another factor is the fact that in the electrochemical series nickel is only moderately negative with respect to H⁺/H₂ equilibrium. This means that in practice, the rate of dissolution of nickel in acidic solutions is slow in the absence of oxidants more powerful than H⁺ or of a substance capable of making the anodic reaction kinetically easy. In HNO₃ solutions, there still exists the problem regarding the state of oxidation of anodically and spontaneously passivated nickel [2–4]. In concentrated HNO₃ solutions, nickel suddenly becomes protected against corrosion. Such a passive state can be obtained when nickel is anodically polarized in acid and neutral solutions. The behavior of nickel in a wide range of HNO₃ concentrations was examined by Abd El Haleem et al. [5], using the thermometric technique supported by weight loss and potential measurements. Dissolution of nickel in dilute HNO₃ solutions was assumed to take place according to an autocatalytic mechanism involved in the formation of HNO₂, while passivation occurs in solutions >9.4 M HNO₃. Using the techniques of electrochemical polarization of nickel in highly concentrated HNO₃ [2], Ni(NO₃)₂·4H₂O is formed in the beginning of the passivation process, changes to NiO₂, and then slowly transforms to NiO. In dilute HNO₃ solutions, however, Kumar et al. [4], indicated that only a single oxide film formed on the nickel surface during anodic oxidation.

The corrosion behavior of nickel in acid baths in plating, electrowinning and pickling process is of industrial concern. Although the mechanism of corrosion and inhibition of nickel has been studied in different media [6–8], studies in nitric acid in the presence of organic molecules are rare [9–11].

Kumar et al. [4] studied the corrosion inhibition of nickel using different thiones in 4% nitric acid at different temperatures. The inhibition efficiencies of thiones are determined by the electrochemical technique (potential decay experiments) and carried out to determine the relative stability of the passive film formed on the nickel surface in the presence and absence of thiones. The electrochemical investigations of nickel in a wide range of concentrations (1–14.6 M) of nitric acid were studied by various electrochemical techniques as well as the chemical (weight loss) method [2].
Khaled and Amin [10] studied corrosion and corrosion inhibition behavior of nickel electrode in 1.0 M HNO₃ in the absence and presence of some selected piperidine derivatives. Corrosion inhibition efficiency of the selected piperidines was studied computationally by the molecular dynamics simulation and quantum chemical calculations and electrochemically by Tafel and impedance methods. The results indicate a strong dependence of the inhibition performance on the nature of the metal surface, in addition to the structural effects of piperidines. The nickel/inhibitor/solvent interfaces were simulated and the charges on the inhibitor molecules as well as their structural parameters were calculated in the presence of solvent effects. Quantum chemical calculations based on the ab initio method were performed to determine the relationship between the molecular structure of piperidines and their inhibition efficiency.

The aim of this study is to investigate the inhibitive properties of three selected thiosemicarbazone derivatives namely 3-pyridinecarboxaldehyde thiosemicarbazone (META), isonicotinaldehyde thiosemicarbazone (PARA) and 2-pyridinecarboxaldehyde thiosemicarbazone (ORTHO) on the inhibition of nickel corrosion in 1.0 M HNO₃ solutions using electrochemical techniques (polarization and impedance) as well as the Metropolis Monte Carlo method to search for adsorption configurations of the studied compounds on Ni (1 1 1) surface to find the low energy adsorption sites on the nickel surface and to investigate the preferential adsorption of the studied thiosemicarbazone derivatives.

2. Experimental procedures

Experiments were performed on nickel electrode with 99.999% purity (Johnson Matthey Chemicals). The nickel rod was welded to iron wire for electrical connection and mounted in Teflon with a flat disc shaped surface of (0.28 cm²) geometric area to contact the test solution. Prior to each experiment, the nickel electrode was polished using different grit sizes emery papers up to 4/0 grit size to remove the corrosion products, if any, formed on the surface. The nickel electrode was cleaned in 18 MΩ bi-distilled water and immediately immersed in the test solution. Ultrasound cleaning was performed for 5 min and subsequently rinsed in acetone and bi-distilled water and immediately immersed in the test solution. The thiosemicarbazone derivatives used in this study are as follow:

![3-Pyridinecarboxaldehyde thiosemicarbazone (META)](image)

![Isonicotinaldehyde thiosemicarbazone (PARA)](image)

![2-Pyridinecarboxaldehyde thiosemicarbazone (ORTHO)](image)

All of these compounds were obtained from Aldrich chemical co. They were added to the 1.0 M HNO₃ (Fisher Scientific) with pre-treatment at concentrations of 10⁻⁴, 10⁻³, 5 × 10⁻³, and 10⁻² M. The electrode was immersed in these solutions for 1 h before starting measurements; this was the time necessary to reach a quasi-stationary value for the open-circuit potential.

Electrochemical measurements were carried out in a conventional electrochemical cell containing three compartments for working (with an exposed area of 0.28 cm²), a platinum foil (1.0 cm²) as counter electrode and a reference electrode. A Luggin–Haber capillary was also included in the design. The tip of the Luggin capillary was made very close to the surface of the working electrode to minimize IR drop. The reference electrode was a saturated calomel electrode (SCE) used directly in contact with the working solution. The experiments were conducted in a 150 cm³ volume cell, open to air, at 25 °C ± 1 using a temperature control water bath. All potential values were reported in volt (SCE).

Each run was carried out in stagnant aerated 1.0 M HNO₃ solutions without and with various concentrations (10⁻⁴–10⁻² M) of thiosemicarbazone derivatives.

Polarization measurements were carried out starting from a cathodic potential of −0.27 V to an anodic potential of +0.2 V at a sweep rate of 0.1 mV s⁻¹. Impedance measurements were carried out using AC signals of amplitude 5.0 mV peak to peak at the open-circuit potential in the frequency range 30 kHz to 1.0 mHz.

Measurements were performed with a 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 impedance measurements to calculate the corrosion current and the Tafel constants along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.

3. Computational details

In the current study, thiosemicarbazone derivatives have been simulated as adsorbate on Ni (1 1 1) substrate to find the low energy adsorption sites on the nickel surface and to investigate the preferential adsorption of the studied thiosemicarbazone derivatives. The aim of the computational study is to identify possible adsorption configurations by carrying out Monte Carlo searches of the configurational space of the nickel/inhibitor system as the temperature is slowly decreased. The adsorbates were three different thiosemicarbazone derivatives constructed and their energy was optimized using Forcite classical simulation engine [12]. The geometry optimization process is carried out using an iterative process, in which the atomic coordinates are adjusted until the total energy of a structure is minimized, i.e., it corresponds to a local minimum in the potential energy surface. Geometry optimization is based on reducing the magnitude of calculated forces until they become smaller than defined convergence tolerances. The forces on the atoms in the thiosemicarbazone derivatives are calculated from the potential energy expression and will, therefore, depend on the force field that is selected.

The molecular dynamics (MD) simulations as well as quantum chemical calculations were performed using the Materials Studio software [13]. The MD simulation of the interaction between thiosemicarbazone derivatives and Ni (1 1 1) surface was carried out in a simulation box (17.38 Å × 17.38 Å × 44.57 Å) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary boundary effects. The Ni (1 1 1) surface was first built and relaxed by minimizing its energy using molecular mechanics, then the surface area of Ni (1 1 1) was increased and its periodicity is changed by constructing a super cell, and then a vacuum slab with 50 Å thicknesses was built on the Ni (1 1 1) surface. The number of layers in the structure was chosen so that the depth of the surface is greater than the non-bond cutoff used in calcula-
tion. Using 6 layers of nickel atoms gives a sufficient depth that the inhibitor molecules will only be involved in non-bond interactions with nickel atoms in the layers of the surface, without increasing the calculation time unreasonably. This structure then converted to have 3D periodicity. As 3D periodic boundary conditions are used, it is important that the size of the vacuum slab is great enough (50 Å) that the non-bond calculations for the adsorbate does not interact with the periodic image of the bottom layer of atoms in the surface. After minimizing the Ni (1 1 1) surface and thiosemicarbazone derivatives molecules, the corrosion system will be built by layer builder to place the inhibitor molecules on Ni (1 1 1) surface, and thus provide access to the energetic of the adsorption and its effects on the inhibition efficiencies of thiosemicarbazone derivatives [14].

The binding energy between thiosemicarbazone derivatives and Ni (1 1 1) surface were calculated using the following equation [15]:

$$E_{\text{binding}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhibitor}})$$

where $E_{\text{total}}$ is the total energy of the surface and inhibitor, $E_{\text{surface}}$ is the energy of the Ni (1 1 1) surface without the inhibitor, and $E_{\text{inhibitor}}$ is the energy of the inhibitor without the surface.

4. Results and discussion

4.1. Tafel polarization

Tafel polarization curves recorded for nickel electrode in aerated 1.0 M HNO₃ solutions in the absence and presence of different thiosemicarbazone derivatives concentrations ($10^{-4}$, $10^{-3}$, $5 \times 10^{-3}$, and $10^{-2}$ M) at 25 °C are shown in Fig. 1. It is obvious that the nickel electrode immersed in nitric acid solution displays a cathodic region of Tafel behavior. However, the anodic polarization curve does not display an extensive Tafel region, instead it shows a plateau that goes with primary passivity, and arises after oxygen evolution [16]. The existence of passivation in conjunction with a dissolution reaction does not result in a well-defined experimental anodic Tafel region. Therefore, due to absence of linearity in anodic branch, accurate evaluation of the anodic Tafel slope ($\beta_a$) by Tafel extrapolation of the anodic branch is impossible [17–20].

There is, therefore an uncertainty and source of error in the numerical values of the anodic Tafel slope ($\beta_a$); the reason why we did not introduce $\beta_a$ values recorded by the software. It has been shown that in the Tafel extrapolation method, use of both the anodic and cathodic Tafel regions is preferred over the use of only one Tafel region [21]. However, the corrosion rate can also be determined by Tafel extrapolation of either the cathodic or anodic polarization curve alone. If only one polarization curve alone is used, it is generally the cathodic curve which usually produces a longer and better defined Tafel region in Fig. 1. Detailed description of the method of determination of corrosion current density by this method has been presented elsewhere [22,23].

Although the anodic dissolution of nickel in nitric acid is well described in the literature [24–26], there is no means agreement either on the mechanism of passivation of nickel or on the composition and thickness of the passive layer [2]. Generally, the important feature is that the nature of the anion of the electrolyte is a determining parameter in the anodic dissolution of nickel [32]. Analyzing the form of polarization curves in Fig. 1, we can see some different phases of polarization. First, the anodic polarization curve corresponds to the electrochemical generation of nickel oxide and/or nitrates. Several reaction schemes for interpreting the anodic dissolution/passivation of nickel in dilute nitric acid have been presented in the literature [2,4,27]. All the electron and mass transfers are made through the intermediate of adsorbed species at the reactive interface; so we propose only one general model where all the reactions may be produced by anion (NO₃⁻ or OH⁻). On a nickel atom, one anion NO₃⁻ or OH⁻ may be adsorbed and the surface active anions are believed to participate directly in the dissolution process by adsorption at the nickel surface.
As an example, the dissolution of nickel in presence of nitrate anion \((A = NO_3^-)\) can be described by the following set of equations [16], where \(k_1\) and \(k_2\) are rate constants
\[
\begin{align*}
Ni + A^- & \rightarrow Ni-A_{ads} + e \\
Ni-A_{ads} & \rightarrow Ni^{2+} + e \\
Ni-A_{ads} & \rightarrow Ni^{2+}_{ads} + e
\end{align*}
\] (2) (3) (4)

Eq. (4) is a chemical reaction, whereas Eqs. (2) and (3) are electrochemical reactions which involve the adsorbed intermediate species \(Ni-A_{ads}\); this intermediate occupies a fraction \(\theta\) of the electrode area.

On the other hand, it is known [27] that the series of the cathodic reactions of the reduction of nitric acid occurs in the following way:
\[
NO_3^- \rightarrow NO_2 \rightarrow NO \rightarrow N_2 \rightarrow \cdots
\]

Some authors [28] show that the reduction of nitric acid on nickel electrode can even lead to the formation of ammonia.

The hydrogen evolution reaction (h.e.r.) and the oxygen reduction reaction are the two most important cathodic processes in the corrosion of nickel in aerated nitric acid solutions, and this is due to the fact that hydrogen ions and water molecules are invariably present in aqueous solution, and since most aqueous solutions are in contact with the atmosphere, dissolved oxygen molecules will normally be present.

In the complete absence of oxygen, or any other oxidizing species, the h.e.r. will be the only cathodic process possible, and if the anodic reaction is only slightly polarized the rate will be determined by the kinetics of the h.e.r. on the particular metal under consideration (cathodic control). However, in the present study where dissolved oxygen is present, and presence of 1.0 M nitric acid both cathodic reactions will be possible, and the rate of the corrosion reaction will depend upon a variety of factors such as the reversible potential of the Ni/Ni^{2+} system, the pH of the solution, the concentration of oxygen, the kinetics of the h.e.r. and the oxygen reduction reaction on the nickel electrode, temperature, etc. In general, the contribution made by the h.e.r. will increase in significance with decrease in pH, but this too will depend upon the nature of the metal and metal oxide. It should also be noted that both reactions will result in an increase in pH in the diffusion layer.

The influence of the anodic and cathodic reactions on the behavior of nickel in nitric acid has been investigated by addition of thiosemicarbazone derivatives to the solution. Addition of thiosemicarbazone derivatives retards the anodic dissolution and cathodic reduction reactions that occurs on nickel surface in 1.0 M HNO_3. Thiosemicarbazone derivatives destroy completely nitrous acid which is always present in small amounts in nitric acid [29] and which increases by the reduction of nitric acid. The values of the corrosion current density \(i_{corr}\) for nickel corrosion reaction without and with thiosemicarbazone derivatives were determined by extrapolation of the cathodic Tafel lines to the corrosion potential \(E_{corr}\). Table 1 represents the influence of thiosemicarbazone derivatives on the corrosion kinetic parameters. As it can be seen from Fig. 1, the anodic and cathodic reactions are affected. Thiosemicarbazone derivatives are thus mixed-type inhibitors, meaning that the addition of these compounds to nitric acid solutions reduces the anodic dissolution of nickel, corresponding to a noticeable decrease in the current densities of the passivation plateau, and also retards the cathodic reactions that occur on the nickel surface.

Electrochemical parameters associated with polarization measurements, such as corrosion potential \(E_{corr}\), corrosion currents densities \(i_{corr}\) and cathodic Tafel slope \(\beta_c\), are listed in Table 1 as a function of thiosemicarbazone derivatives concentration. As it can be seen, the corrosion potential \(E_{corr}\) have no definite shift and \(i_{corr}\) decreases when the concentration of thiosemicarbazone derivatives is increased. Absence of significant change in the cathodic Tafel slope \(\beta_c\) in the presence of thiosemicarbazone derivatives indicates that the corrosion mechanism is not changed after adding the thiosemicarbazone derivatives, and the inhibition effect is due to simple adsorption. These findings also indicate that the cathodic reactions are under activation-controlled and the addition of thiosemicarbazone derivatives does not affect the mechanism of the corrosion process [30].

It follows from the data of Table 1 that, at 25 °C ± 1, the inhibition efficiency increases with increasing thiosemicarbazone derivatives concentrations. It is seen that thiosemicarbazone derivatives has inhibiting properties at all studied concentrations and the values of inhibition efficiency \(\pi_p(%)\) increase as the thiosemicarbazone derivatives concentrations increase.

The percentage of inhibition efficiency \(\pi_p(\%)\) were calculated using the following equation:
\[
\pi_p(\%) = \left(1 - \frac{i_{corr}}{i_{corr}^o}\right) \times 100
\] (5)
where \(i_{corr}^o\) and \(i_{corr}\) are corrosion current densities in the absence and presence of inhibitors, respectively. From the results in Table 1, it can be observed that the values of corrosion current density \(i_{corr}\) of nickel in the inhibitor-containing solutions were lower than those for the inhibitor-free solution. The corrosion current densities at all inhibitor concentrations are decreased in the order of META > PARA > ORTHO.

<table>
<thead>
<tr>
<th>Inhibitor type</th>
<th>[Inhib]</th>
<th>M</th>
<th>(\beta_c/\text{mV} \text{ dec}^{-1})</th>
<th>(-E_{corr}/\text{mV (SCE)})</th>
<th>(i_{corr}/\mu\text{A cm}^{-2})</th>
<th>(\pi_p(%))</th>
<th>Corrosion rate/ mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORTHO</td>
<td>Blank</td>
<td>169.1</td>
<td>19.8</td>
<td>527</td>
<td>223.7</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>10^-1</td>
<td>168.8</td>
<td>12</td>
<td>437.2</td>
<td>17.0</td>
<td>185.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^-2</td>
<td>168.8</td>
<td>16</td>
<td>251.3</td>
<td>52.3</td>
<td>106.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 x 10^-3</td>
<td>169.5</td>
<td>17</td>
<td>136.5</td>
<td>74.1</td>
<td>57.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^-3</td>
<td>167.3</td>
<td>19.2</td>
<td>82.2</td>
<td>84.4</td>
<td>34.47</td>
<td></td>
</tr>
<tr>
<td>PARA</td>
<td>10^-4</td>
<td>161.2</td>
<td>25.3</td>
<td>395.7</td>
<td>24.9</td>
<td>167.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^-3</td>
<td>169.5</td>
<td>28.5</td>
<td>235.5</td>
<td>55.3</td>
<td>99.95</td>
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<tr>
<td></td>
<td>5 x 10^-3</td>
<td>168.5</td>
<td>21.5</td>
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<td>81.5</td>
<td>40.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^-2</td>
<td>171.1</td>
<td>18.3</td>
<td>34.3</td>
<td>93.5</td>
<td>14.75</td>
<td></td>
</tr>
<tr>
<td>META</td>
<td>10^-4</td>
<td>171.0</td>
<td>11.8</td>
<td>244.1</td>
<td>53.7</td>
<td>103.0</td>
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<tr>
<td></td>
<td>10^-3</td>
<td>171.8</td>
<td>13.1</td>
<td>123.8</td>
<td>76.5</td>
<td>52.22</td>
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<tr>
<td></td>
<td>5 x 10^-3</td>
<td>169.0</td>
<td>12.4</td>
<td>56.4</td>
<td>89.3</td>
<td>23.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10^-2</td>
<td>170.8</td>
<td>12.6</td>
<td>20.76</td>
<td>96.1</td>
<td>8.79</td>
<td></td>
</tr>
</tbody>
</table>
Moreover, the diameter of the first semicircle increases gradually with the increase of the thiosemicarbazone derivatives concentration from $10^{-4}$ to $10^{-2}$ M.

As usually indicated in the EIS study, on one hand, the HF capacitive loop is related to the charge transfer process of the metal corrosion and the double layer behavior, the MF capacitive loop is connected with the adsorption process of the thiosemicarbazone derivatives on the nickel surface which increased with the increase of the inhibitor concentrations, and the LF inductive loop may be attributed to the relaxation processes obtained by adsorption of inhibitor on the electrode surface [31]. The inductive behavior at low frequency is probably due to the consequence of the layer stabilization byproducts of the corrosion reaction on the electrode surface, involving inhibitor molecules and their reactive products [32]. It may also be attributed to the re-dissolution of passivated surface. On the other hand, as is seen, the HF capacitance loops in Fig. 4 enlarge as the increase of ORTHO and PARA derivatives concentrations, respectively. It means that the inhibition efficiency is proportional to the increment of inhibitor concentration, namely, the greater the inhibitor concentration, the higher the inhibition efficiency.

The effect of inhibitor concentration on the impedance behavior of nickel in 1.0 M HNO$_3$ solution at 25 °C is presented in Fig. 2. The curves show a similar type of Nyquist plot for nickel in the presence of various concentrations of ORTHO and PARA. As seen from Fig. 2, the Nyquist plots contain a depressed semicircles, with the centre below the real x-axis, which sizes are increasing by increasing the inhibitor concentration, indicating that the corrosion is mainly a charge transfer process [33]. A loop is also seen at low frequencies which could be arising from the adsorbed intermediate products on the nickel surface [34]. It is worth noting that the change in the concentration of thiosemicarbazone derivatives did not alter the style of the impedance curves, suggesting a similar mechanism of inhibition involved.

In case of META derivative, two capacitive loops with two time constants, first at HF with high polarization resistance ($R_1$) and the other at low frequency with small polarization resistance ($R_2$) appear. The total polarization resistance $R_p$ equals ($R_1 + R_2$). Impedance spectra of META derivative shown in Fig. 2 can be interpreted by using two time constants model as presented in Fig. 3b. In case of META derivatives, the first time constant was shown at high frequency and was related to an external porous layer, whereas the second time constant, at lower frequencies, was attributed to a more resistive internal layer. In this case, the transfer function is the sum of the corresponding layer impedance [35].

$$Z(S)^{-1} = V(S) = \theta V_L(S) + (1 - \theta)V_{corr}(S)$$

where $V_L(S)$ is the layer admittance and $V_{corr}(S)$ denotes the admittance of the corrosion process which occurs at the nickel/nitric acid interface at the bottom of the “virtual pores” within the film [35].

It is essential to develop the appropriate physical models which can then be used to fit the experimental data and extract the parameters which characterize the corrosion process. Fig. 3 shows the equivalent circuit models used to fit the experimental impedance data of nickel in 1.0 M HNO$_3$ containing inhibitors, in this case $R_p$ refers to the solution resistance, $CPE$ the constant phase element, $R$ the polarization resistance, $L$ the inductance. Inductivity $L$ may be correlated with a slow low frequency intermediate process [36]. It should be noticed that the depression of the large semicircles (i.e. rather than perfect semicircles) in the complex impedance plane of the Nyquist plots, with the centre under the real axis, appears in Fig. 2. Deviation of this kind, often referred to as frequency dispersion, was attributed to roughness and inhomogeneities of the solid surface. Therefore, a constant phase element (CPE) instead of a capacitive element is used in Fig. 3 to get a more accurate fit of experimental data sets using generally more complicated equiva-

### 4.2. Electrochemical impedance spectroscopy

Fig. 2 shows the impedance spectra of nickel in 1.0 M HNO$_3$ solution in the absence and presence of different concentrations of thiosemicarbazone derivatives (the same solutions as used in polarization measurements). As can be seen in Fig. 2, for the derivatives ORTHO and PARA, the complex impedance diagrams consist of three time constants, i.e., a large capacitive loop at high frequency (HF), a small capacitive loop at medium frequency (MF) and a small inductive one at low frequency (LF) values.
Fig. 3. Equivalent circuits used to model impedance data for nickel in 1.0 M HNO₃ solutions (a) equivalent circuit for derivatives ORTHO and PARA, (b) equivalent circuit for derivative META.

Table 2

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>( R_0/\Omega \text{cm}^2 )</th>
<th>( R_1/\Omega \text{cm}^2 )</th>
<th>( \text{CPE}_1/\mu\Omega^{-1} \text{cm}^{-2} \text{S}^n )</th>
<th>( n_1 )</th>
<th>( R_2/\Omega \text{cm}^2 )</th>
<th>( \text{CPE}_2/\mu\Omega^{-1} \text{cm}^{-2} \text{S}^n )</th>
<th>( n_2 )</th>
<th>( L/H \text{cm}^{-2} )</th>
<th>( R_3/\Omega \text{cm}^2 )</th>
<th>( \eta% )</th>
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<td>0.6</td>
<td>32</td>
<td>15.7</td>
<td>0.89</td>
<td>1.7</td>
<td>5.9</td>
<td>0.75</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ORTHO</td>
<td>10^{-4}</td>
<td>1.2</td>
<td>47</td>
<td>30</td>
<td>0.76</td>
<td>20</td>
<td>0.87</td>
<td>11</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>10^{-3}</td>
<td>1.1</td>
<td>77</td>
<td>26</td>
<td>0.77</td>
<td>25</td>
<td>0.88</td>
<td>10</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>5 x 10^{-3}</td>
<td>1.5</td>
<td>170</td>
<td>20</td>
<td>0.76</td>
<td>30</td>
<td>0.89</td>
<td>7</td>
<td>8</td>
<td>3.5</td>
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<td></td>
<td>10^{-2}</td>
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</tr>
<tr>
<td>PARA</td>
<td>10^{-4}</td>
<td>1.3</td>
<td>55</td>
<td>40</td>
<td>0.77</td>
<td>15</td>
<td>0.75</td>
<td>10</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>10^{-3}</td>
<td>1.5</td>
<td>80</td>
<td>33</td>
<td>0.76</td>
<td>19</td>
<td>0.77</td>
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<td>11</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>5 x 10^{-3}</td>
<td>2.1</td>
<td>290</td>
<td>30</td>
<td>0.77</td>
<td>23</td>
<td>0.89</td>
<td>25</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>10^{-2}</td>
<td>2.3</td>
<td>695</td>
<td>25</td>
<td>0.77</td>
<td>30</td>
<td>0.87</td>
<td>36</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>META</td>
<td>10^{-4}</td>
<td>1.1</td>
<td>71</td>
<td>40</td>
<td>0.76</td>
<td>30</td>
<td>0.77</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10^{-3}</td>
<td>1.3</td>
<td>281</td>
<td>33</td>
<td>0.77</td>
<td>33</td>
<td>0.78</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>5 x 10^{-3}</td>
<td>2.01</td>
<td>652</td>
<td>22</td>
<td>0.8</td>
<td>35</td>
<td>0.786</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>10^{-2}</td>
<td>2.2</td>
<td>1230</td>
<td>15</td>
<td>0.74</td>
<td>40</td>
<td>0.76</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Total energy (kcal mol⁻¹)</th>
<th>Adsorption energy (kcal mol⁻¹)</th>
<th>Rigid adsorption energy (kcal mol⁻¹)</th>
<th>Deformation energy (kcal mol⁻¹)</th>
<th>( dE_{ads}/dN_i ) (kcal mol⁻¹)</th>
<th>Calculated binding energy (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORTHO</td>
<td>−152.39</td>
<td>−574.5</td>
<td>−60.46</td>
<td>−514.0</td>
<td>−574.5</td>
<td>216.5</td>
</tr>
<tr>
<td>PARA</td>
<td>−144.11</td>
<td>−567.85</td>
<td>−60.64</td>
<td>−507.2</td>
<td>−567.85</td>
<td>312.2</td>
</tr>
<tr>
<td>META</td>
<td>−129.81</td>
<td>−566.7</td>
<td>−60.62</td>
<td>−506.08</td>
<td>−566.7</td>
<td>395.6</td>
</tr>
</tbody>
</table>

Tables 2–4 contains all the impedance parameters obtained from the simulation of experimental impedance data for ORTHO, PARA and META, including \( R_n, R_1, R_2, R_3, L \) and CPEs (for the fitting of \( Q = 0.7–0.9 \)). The inhibition efficiency \( (\eta\%) \) is calculated from the following equation [38]:

\[
\eta\% = \left(1 - \frac{1}{R/R_0}\right) \times 100
\]

where \( R_0 \) and \( R \) represents the uninhibited and inhibited polarization resistance (intersection of the low frequency inductive loop

Table 4

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>( E_{HOMO} ) (kcal mol⁻¹)</th>
<th>( E_{LUMO} ) (kcal mol⁻¹)</th>
<th>( \Delta = E_{LUMO} - E_{HOMO} ) (kcal mol⁻¹)</th>
<th>( \mu/(D) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORTHO</td>
<td>−207.3</td>
<td>17.5</td>
<td>224.8</td>
<td>6.2</td>
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<tr>
<td>PARA</td>
<td>−189.3</td>
<td>12.0</td>
<td>201.3</td>
<td>5.2</td>
</tr>
<tr>
<td>META</td>
<td>−181.7</td>
<td>8.1</td>
<td>189.8</td>
<td>4.52</td>
</tr>
</tbody>
</table>
with x-axis in case of ORTHO and PARA and intersection of the low frequency capacitive loop with x-axis in case of META derivatives), respectively. It can be seen from Table 2 that, with the increase of inhibitor concentrations (ORTHO, PARA and META), the inhibition efficiencies increase noticeably, especially the situation of increasing concentration of META derivatives. At the same concentration of inhibitors, the inhibition efficiency of these inhibitors is in the order: META > PARA > ORTHO, which is in consistence with the Tafel polarization results.

4.3. Computational study

Fig. 4 shows the most suitable configuration for adsorption of thiosemicarbazone derivatives on Ni (1 1 1) substrate obtained by adsorption locator module [39,40] in Materials studio [41]. A snapshot of the different adsorption structures and the corresponding calculated adsorption energy is presented in Fig. 5. The adsorption density of thiosemicarbazone derivatives on the Ni (1 1 1) substrate has been presented in Fig. 6. As can be seen from Figs. 4 and 6, that...
the META derivatives show the highest ability to adsorb on Ni surface also, it has the highest binding energy to Ni surface as seen in Table 3.

The outputs and descriptors calculated by the Monte Carlo simulation are presented in Table 3. The parameters presented in Table 3 include total energy, in kcal mol\(^{-1}\), of the substrate–adsorbate configuration. The total energy is defined as the sum of the energies of the adsorbate components, the rigid adsorption energy and the deformation energy. In this study, the substrate energy (nickel surface) is taken as zero. In addition, adsorption energy in kcal mol\(^{-1}\), reports energy released (or required) when the relaxed adsorbate components (thiosemicarbazone derivatives) are adsorbed on the substrate. The adsorption energy is defined as the sum of the rigid adsorption energy and the deformation energy for the adsorbate components. The rigid adsorption energy reports the energy, in kcal mol\(^{-1}\), released (or required) when the unrelaxed adsorbate components (i.e., before the geometry optimization step) are adsorbed on the substrate. The deformation energy reports the energy, in kcal mol\(^{-1}\), released when the adsorbed adsorbate components are relaxed on the substrate surface. Table 3 shows also \((\Delta E_{ads}/\Delta N)\), which reports the energy, in kcal mol\(^{-1}\), of substrate–adsorbate configurations where one of the adsorbate components has been removed. The binding energy introduced in Table 3 calculated from Eq. (1)

As can be seen from Table 3, META gives the maximum adsorption energy found during the simulation process. High values of adsorption energy indicate that META derivative is the most efficient inhibitor. Therefore, the studied molecules are likely to adsorb on the nickel surface to form stable ad layers and protect nickel from corrosion. The binding energies as well as the adsorption energy were found to increase in the order META > PARA > ORTHO.

In Table 4, several quantum-chemical parameters calculated by using DFT method. The HOMO energy can indicate the disposition of the molecule to donate electrons to an appropriated acceptor with empty d molecular orbitals. Also, an increase in the values of \(\Delta E_{HOMO}\) can facilitate the adsorption, and therefore improved inhibition efficiency results [10]. The corrosion rate decrease with increases in HOMO energy (less negative), therefore an increase in the corrosion inhibition is present. Low values of the energy gap \((\Delta E)\) will provide good inhibition efficiencies, because the excitation energy to remove an electron from the last occupied orbital will be low [10,14]. The results show that the META derivative has the lowest energy gap; this agrees with the experimental results that this molecule could have better performance as a corrosion inhibitor. The dipole moment is another way to obtain data on the electronic distribution in a molecule and is one of the properties more used traditionally to discuss and rationalize the structure and reactivity of many chemical systems [23]. It is confirmed in the literature that lower dipole moment \(\mu\) is associated with high inhibition efficiency [23]. According to the quantum chemical calculations, the dipole moment \(\mu\) of META, PARA and ORTHO are 4.52, 5.2 and 6.2, respectively, see Table 4. The lower value calculated for META agrees with the experimentally measured larger adsorption of META as compared with the other two thiosemicarbazone derivatives.

It is probably that the parts of the molecules with high HOMO density were oriented towards the nickel surface and the adsorption of these inhibitors could be sharing the lone pair electrons of nitrogen atoms and the \(\pi\)-electrons of the aromatic ring. Therefore the electron density on thio-group would determine the effectiveness of this type of inhibitors. In thiosemicarbazone derivatives, the electron density of the nitrogen and sulphur atoms is localized around these atoms. Substitution of pyridyl group for hydrogen leads to the withdrawal of electrons from these atoms and tends to delocalize the charges throughout pyridyl ring and hence lowers its basicity.

4.4. Mechanism of adsorption

The adsorption of thiosemicarbazone derivatives can be described by two main types of interaction: physical adsorption and chemisorption. Physical adsorption is the result of electrostatic attractive forces between the cationic form of thiosemicarbazone derivatives and the electrically charged nickel surface. Chemisorption process involves charge sharing or charge-transfer from the lone pairs of electrons in the thiosemicarbazone derivatives to the vacant d-orbital in the nickel surface to form a coordinate type of a bond. This is possible in case of a positive as well as a negative charge of the surface. The surface charge can be defined by the position of the corrosion potential \((E_{corr})\) with respect to the respective potential of zero charge \((PZC)\). When the difference \(\varphi=(E_{corr}−E_{PZC})\) is negative, the electrode surface acquires a negative net charge and the adsorption of cations is favoured. On the contrary, the adsorption of anions is favoured when \(\varphi\) becomes positive. It has been shown from our previous study [10] where ac impedance studies used to evaluate the potential of zero charge \((PZC)\) from the capacitance \((C_0)\) vs voltage \((E)\) plot [10]. We also, confirmed that the surface charge of nickel in nitric acid solution at the free corrosion potential is negative \((\varphi=−(0.00192)−(0.037)=−0.0562\,mV(SCE))\). The inhibitors under investigations, namely thiosemicarbazone derivatives are organic bases which protonize in an acid medium and form cations (protonated nitrogen atoms).

Physical adsorption might occur between the negative nickel surface and the protonated thiosemicarbazone derivatives. In addition to the physical adsorption, there should be chemical adsorption owing to the coordinate bonds formed between the lone electron pairs of the N-atom in thiosemicarbazone derivatives and the empty orbits of nickel atoms which enhanced the combination intension between the thiosemicarbazone derivatives molecules and electrode surface. The adsorption monolayer of thiosemicarbazone derivatives became compact and adherent to the nickel surface with increasing its concentration, so the
cathodic reduction and anodic dissolution reaction were inhibited extremely.

In the passive region where the surface of the nickel electrode is covered by oxide layer with different composition [2]. This layer according with the finding of Hoare and Wiese [43] about the formation of NiO₂ film which transforms slowly to NiO. On the other hand, it may be possible, according to Korte [44]. That in the beginning of the repassivation process Ni(NO₃)₂ 4H₂O forms which changes to NiO₂ and NiO, respectively.

The presence of oxide layer on the nickel surface encourage the adsorption of the thiosemicarbazone derivatives on the nickel surface via H-bonding.

Literature survey shows that few investigations have shown that adsorption could also occur through hydrogen bonding [45,46].

Adsorption in this case is assisted by hydrogen bond formation between thiosemicarbazone derivatives 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.

5. Conclusions

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

1. The selected thiosemicarbazone derivatives were found to be effective inhibitors for nickel corrosion in 1.0 M HNO₃ 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 increased of the thickness and integrity of the adsorbed thiosemicarbazone derivatives.

5. Computational studies helps to find the most stable adsorption sites for a broad range of materials. This information can help to gain further insight about corrosion system, such as the most likely point of attack for corrosion on a surface, the most stable site for inhibitor adsorption and the binding energy of the adsorbed layer.

References