Theoretical and experimental evaluation of the inhibiting power of 4-amino,5-phenyl-1,2,4-triazole,3-thione against corrosion copper in a neutral chloride environment

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Abstract: In this study, we first developed the synthesis of 4-amino-5-phenyl-1,2,4-triazole-3-thione (APTS) and then its identification based on 1H and 13C NMR spectral data. The product’s ability to prevent copper corrosion in a 3% NaCl solution was then evaluated. This work was carried out by stationary and transient electrochemical techniques, supplemented by a theoretical study. The results obtained showed that the APTS provides good protection of copper in the corrosive environment by the formation of a protective layer adsorbed on the metal surface. The inhibitory efficiency achieved is around 98% for a concentration of 10−3M in inhibitor justifying its protective effect. The theoretical study of the interaction of APTS with metallic copper shows that this inhibitor adsors on the metallic surface by forming chemical bonds between the metal and the inhibitor. This confirms the experimental results.

Keywords: Synthesis; NaCl; Copper corrosion; inhibitor; of 1,2,4-triazole (APTS)

1. Introduction

Heterocyclic compounds are organic products characterized by the presence of oxygen, nitrogen, or sulfur in their structure (Hammouti et al., 2011; Zarrok et al., 2011; Zarrok et al., 2012; Zarrouk et al., 2011; Bendaha et al., 2012; Al Hamzi et al., 2013; Tayebi et al., 2014; Goyal et al., 2018; Nabah et al., 2018; El Issami et al., 2007). In recent years, these compounds have been widely applied in various industrial fields, namely: the chemical and parachemical industry, organic coatings and corrosion inhibitors (Verma et al., 2020; Liu et al. 2022; Haque et al. 2023). The synthesis of heterocyclic compounds such as the derivatives of the Thione triazole has developed well thanks to their practical interests, namely in biology as antioxidants (Tourabi et al., 2013). In the field of electrochemistry, organic inhibitors are used to reinforce the protection of metals and their alloys against corrosion (Gasparac et al., 1999, Benzidia et al., 2022).
The presence of thione and amine groups in heterocyclic compounds increases their inhibitory power against corrosion of copper and its alloys (Milié et al., 2009, Devi et al., 2017). Their inhibitory power has been demonstrated in recent years through their tendency to form complexes with metallic copper (Branzoi et al., 2004, Scherif and Park, 2005, Scherif and Park, 2006, Scherif et al., 2007). These complexes act by forming a protective film insulating the metallic surface from the aggressive medium.

These heterocycles, derived from the triazoles, have found a wide range of applications in protecting against copper corrosion in the neutral chloride environment since their inhibitory properties make them essential for preventing copper deterioration in saline solutions. These compounds play a key role in the maritime industry, where copper is often used in cooling systems and ship hulls. Additionally, triazole derivatives are used in anti-corrosion protection systems for copper pipelines, heat exchangers, electrical and electronic equipment, as well as in the oil and gas industry to protect copper equipment against corrosion due to aggressive environments containing NaCl. Their ability to form protective films on the surface of copper makes them agents of choice for preserving this metal in corrosive conditions. Their use offers a valuable solution for extending the useful life of copper and reducing maintenance costs in various industrial applications (Benhiba et al., 2014, Ben Hmamou et al., 2015).

The compound 4-amino-5-phenyl-1,2,4-triazole-3-thione (APTS), subject of our study, was synthesized and identified in our laboratory and tested as an inhibitor of copper corrosion in a corrosive environment 3%NaCl. The inhibitory capacity of this compound has been evaluated by drawing polarization curves and electrochemical impedance spectroscopy. This research shows that APTS acts by physico-chemical adsorption on the metallic surface of copper. The theoretical research utilizing the DFT and Monte Carlo simulation approach validates the empirically found protective effectiveness of APTS.

2. Methodology

2.1 Medium and material

In this study, the chosen corrosive medium, like an aggressive marine environment, is a 3% NaCl solution prepared from pure solid NaCl dissolved in distilled water. The material used in this study is 99.99% pure copper (Goodfellow).

2.2. Electrochemical instrumentation

A three-electrode configuration with a saturated calomel reference electrode was used to conduct electrochemical testing. The research electrode, which had a surface area of one centimeter and was made of pure copper, was coupled with the auxiliary electrode, which was made of platinum. This sample had been cut into a cylindrical shape and laterally insulated with an epoxy resin. Before the measurements, the surface of the sample was successively smoothed using sandpaper of 600, 1200, 2000 and 2400 grit. Subsequently, it undergoes cleaning using water and acetone, followed by careful drying. The electrochemical measurements were carried out in a Faraday cage using a potentiostat suitable for measuring low currents and high impedances (Biologic SP200). The potential was supplied at a scan rate of 1 mV/s throughout the range of -250 to +250 mV relative to the E_ocp during the potentiodynamic polarization of copper. Using the following formula, the inhibition efficiency (η%) is calculated based on the corrosion current density that corresponds to a given inhibitor concentration.
\[ \eta(\%) = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \times 100 \]  \hspace{1cm} \text{Eqn. 1} 

With
- \( i_{\text{corr}} \): Corrosion current density excluding APTS.
- \( i_{\text{corr(inh)}} \): Corrosion current density with APTS

The experiments that followed used electrochemical impedance spectroscopy (EIS). The starting potential was set at stable E\text{ocp} levels, the excitation signal was a sinusoidal AC potential of 5 mV, and the frequency range covered was 10\(^5\) Hz to 10\(^{-2}\) Hz. EC-Lab software was used to help fit and analyze the impedance spectrum using appropriate comparable circuits. Based on the EIS measurement, the inhibitor's inhibition effectiveness (\(\eta\)) is calculated using the formula below:

\[ \eta(\%) = \frac{R_{t(inh)} - R_{t(0)}}{R_{t(inh)}} \times 100 \]  \hspace{1cm} \text{Eqn. 2} 

With
- \( R_{t(inh)} \): Resistance to charge transfer with APTS.
- \( R_{t(0)} \): Resistance to charge transfer without APTS.

2.3 Inhibitor

The product tested as an inhibitor is 4-amino-5-phenyl-1,2,4-triazole-3-thione (APTS). This product was synthesized in two steps according to the following reaction (Chebabe et al. 2014):

\[
\text{PhCl} + \text{H}_2\text{N-NH-C-NH}_2 \rightarrow \text{PhC-NH-NH-C-NH-NH}_2
\]

To reduce the time and improve the yield of the reaction, we have developed a new way of synthesizing this product in a single step according to the following equation:

\[
\text{PhCOCH}_3 + \text{H}_2\text{N-NH-C-NH}_2 \rightarrow \text{PhN-NH-C-NH}_2
\]

The product, seized with a yield of 92%, is identified and characterized based on \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR:
- \(^1\text{H}\) NMR (500MHz, DMSO-D6): 7.51–7.53 (m, 2H, C6H5); 4.86 (s, 2H, NH2); 11.17 (s, 1H, NH).
• $^{13}$C NMR (125MHz, DMSO-D6): (C phenyl): 128.4-128.2; 128.2-128.6; 128.6-130.2 ppm; (C imine): 148.9 ppm; (C thioamide): 181.8 ppm.

2.4 Quantum chemical calculation

2.4.1 DFT calculations

All geometric structures were fully optimized using DFT method with DMol$^3$ code in Materials Studio 2017 software. The calculation of exchange-correlation energy involved the application of the generalized gradient approximation (GGA) with the PBE functional (Kova et al. 2011). The valence electron function was expanded into numerical atomic orbitals using a double zeta basis set with a polarization function (DNP). It's worth noting that the DNP basis set, in addition to being of a comparable size to Gaussian 6-31 G**, has proven to be more precise (Hehre et al. 1986, Benedek et al. 2005). To enhance computational efficiency, a Fermi smear of 0.005 Ha and a genuine spatial threshold of 4.4 were utilized. The explanation of the interaction between inhibitory molecules and ($E_{\text{HOMO}}$), the lowest unoccupied molecular orbital energy ($E_{\text{LUMO}}$), the energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), the ionization potential ($I$= - $E_{\text{HOMO}}$), and the electron affinity ($A$= -$E_{\text{LUMO}}$) defined according to the DFT-Koopmans theorem, the overall hardness ($\eta$), the electronegativity($\chi$), and the electron transfer fraction ($\Delta N$) as expressed below were analyzed (Janak 1978, Stowasser et al. 1999).

$$\chi = \frac{I + A}{2} \quad \text{Eqn. 3}$$

$$\eta = \frac{I - A}{2} \quad \text{Eqn. 4}$$

$$\Delta N = \frac{\chi_{\text{Cu}} - \chi_{\text{inh}}}{2(\eta_{\text{Cu}} - \eta_{\text{inh}})} \quad \text{Eqn. 5}$$

Here, $\chi_{\text{Cu}}$ and $\chi_{\text{inh}}$ stand for the absolute electronegativity of the inhibitor molecule and copper, respectively, while $\eta_{\text{Cu}}$ and $\eta_{\text{inh}}$ stand for the absolute hardness of the inhibitor molecule and copper, respectively. The assessment of the localized reactivity of the APTS molecule after optimization was accomplished using Fukui indices (Olasunkanmi et al. 2016). This analysis reveals the regions of reactivity in the molecule, highlighting the specific atoms responsible for nucleophilic and electrophilic interactions. The electrophilic and nucleophilic Fukui functions can be defined as follows (Mi et al. 2015):

$$f^+ = q_i (N+1) - q_i (N) \text{ (In the context of nucleophilic reactivity)} \quad \text{Eqn. 6}$$

$$f^- = q_i (N) - q_i (N-1) \text{ (In the context of electrophilic reactivity)} \quad \text{Eqn. 7}$$

The terms $q_i (N+1), q_i (N),$ and $q_i (N-1)$ designate the charges of cations, neutral species, and anions, respectively. The Fukui indices $f^-$ and $f^+$ denote the positions within the molecule where nucleophilic and electrophilic characteristics are observed in the atoms (El yaktini, et al. 2018).

2.4.2 Monte-Carlo simulation (MC)

All simulations of MC are employed the Material Studio 7.0 software using Forcite code. To create the simulation system, Cu was imported in cleavage on a surface following the (111) planes with a fractional thickness of 5.0 building the supercell (7 x 7). The unit cell has been optimized using the Forcite module. After that, a 60 Å thick vacuum slab was built. A supercell, of size $a = 30.678 \text{ Å}, b =$
25.342 Å and c = 60.044 Å, containing 200 H₂O, 3Na⁺, 3Cl⁻ and a molecule of tested, was created. The simulation was performed in a (30.678 × 25.342 ×71.966) Å³ simulation box, employing a discovery module with a time step of 1 femtosecond and a simulation duration of 5 picoseconds, conducted at 298 K. COMPASS (Molecular potentials have been optimized in the condensed phase for use in atomic simulation studies) force field used to perform structural optimization of all components of the system under study.

3. Results and discussion

3.1 Stationary measurements

The cathodic and anodic polarization curves of the copper electrode are shown in Figure 1. These graphs were produced after the electrode was submerged for an hour at the corrosion potential in a 3% NaCl solution containing various APTS concentrations.

![Figure 1](Current-voltage curves for both cathodic and anodic processes of copper in a 3% NaCl solution, without and with various concentrations of APTS.)

In the absence of APTS, the cathodic curve reveals a rise in current density in the vicinity of the corrosion potential. The curve shows a tendency to stabilize forming a current plateau; this can be ascribed to the diffusion of oxygen that has dissolved in the solution. The corrosion kinetics are governed by oxygen diffusion, as described in the following reaction (Ma al. 2002, Mangalam al. 2009, Qiang al. 2017, Zouarhi al. 2019):

\[
\text{O}_2 + 2 \text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{HO}^- \quad \text{Eqn. 8}
\]

When APTS is present in the medium, the cathodic polarization curves show a positive shift in the corrosion potential along with a notable reduction in current density as the inhibitor concentration increases. This finding demonstrates how APTS prevents copper corrosion in a 3% NaCl solution.

In the cathodic region, the current density variation, when represented on a semi-logarithmic scale, demonstrates a linear correlation, which is indicative of the Taffelian domain. This shows that the addition of the inhibitor acts on the kinetics of the cathodic reaction leading to a change in the corrosion mechanism (Damej al. 2015).

The anodic polarization plot for copper in the 3% NaCl solution shows a swift surge in current density in the vicinity of the corrosion potential. This reflects the anodic oxidation of copper in accordance with the subsequent reaction:

\[
\text{Cu} \rightleftharpoons \text{Cu}^+ + \text{e}^- \quad \text{Eqn. 9}
\]
The chloride ions present in the medium react with Cu$^+$ to form CuCl which are transformed into soluble CuCl$_2$, better protecting the metal according to the following two reactions (Tracheli et al. 2002, Damej et al. 2015):

\[
\begin{align*}
\text{Cu} + \text{Cl}^- & \rightleftharpoons \text{CuCl}_{\text{ads}} + e^- \quad \text{Eqn. 10} \\
\text{CuCl}_{\text{ads}} + \text{Cl}^- & \rightleftharpoons \text{CuCl}_2 \quad \text{Eqn. 11}
\end{align*}
\]

The polarization curve indicates the presence of a current plateau at higher anodic potentials. The plateau's limit value is about 10 mA cm$^{-2}$, which is a very high number that suggests copper passivation. Therefore, the production of corrosion products is attributed to this plateau.

Incorporating the APTS inhibitor at varying concentrations into a corrosive medium result in a substantial alteration in the morphology of the polarization curves, accompanied by a marked reduction in current density and an elevation of the corrosion potential.

For the 5×10$^{-4}$ and 10$^{-3}$ M concentrations, a pseudo current level appears, the value of which is around 5 µA cm$^{-2}$, attributed to the creation of an inhibiting layer (film) which forms on the surface of the metal protective against aggressive ions (Almutairi et al. 2018). The breakdown of the film generated on the surface of the copper electrode is shown by the polarization curves at higher anodic potentials, which correspond with the control (Srhiri et al. 2000).

The electrochemical properties derived from the copper polarization curves in a 3% NaCl solution are displayed in Table 1, which also includes the scenarios with and without the APTS inhibitor at different doses.

**Table 1.** The copper's electrochemical properties in a 3% NaCl solution in connection to different APTS concentrations.

<table>
<thead>
<tr>
<th>[APTS] (M)</th>
<th>$E_{\text{corr}}$ (V$_{\text{SCE}}$)</th>
<th>$i_{\text{corr}}$ (µA cm$^{-2}$)</th>
<th>$\beta_c$ (mV dec$^{-1}$)</th>
<th>$E_{\text{corr}}$ (V$_{\text{SCE}}$)</th>
<th>$i_{\text{corr}}$ (µA cm$^{-2}$)</th>
<th>$\beta_a$ (mV dec$^{-1}$)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.282</td>
<td>21.03</td>
<td>-175.2</td>
<td>-0.283</td>
<td>21.13</td>
<td>275.4</td>
<td>------</td>
</tr>
<tr>
<td>5×10$^{-5}$</td>
<td>-0.195</td>
<td>2.77</td>
<td>-147.7</td>
<td>-0.190</td>
<td>2.61</td>
<td>190.0</td>
<td>87.1</td>
</tr>
<tr>
<td>1×10$^{-4}$</td>
<td>-0.151</td>
<td>1.43</td>
<td>-137.8</td>
<td>-0.162</td>
<td>1.32</td>
<td>152.0</td>
<td>93.3</td>
</tr>
<tr>
<td>5×10$^{-4}$</td>
<td>-0.131</td>
<td>0.83</td>
<td>-133.0</td>
<td>-0.140</td>
<td>0.76</td>
<td>143.8</td>
<td>96.1</td>
</tr>
<tr>
<td>1×10$^{-3}$</td>
<td>-0.128</td>
<td>0.68</td>
<td>-129.8</td>
<td>-0.134</td>
<td>0.61</td>
<td>138.9</td>
<td>97.7</td>
</tr>
</tbody>
</table>

When the inhibitor concentration is increased, the corrosion potential shifts in the anodic direction and the corrosion current density significantly decreases, according to an analysis of the data in the table. In the presence of 10$^{-3}$ M APTS, the current density drops from 21.02 µA cm$^{-2}$ in the absence of the inhibitor to 0.68 µA cm$^{-2}$, demonstrating the inhibitor's ability to prevent copper corrosion in the corrosive solution. The anodic slopes undergo alterations due to the establishment of a pseudo current plateau at concentrations of 5×10$^{-4}$ and 10$^{-3}$ M, whilst the cathodic slopes show minimal fluctuations. The aforementioned behavior might be interpreted as the result of the inhibitor adhering to the metal surface and creating a shielding layer.

These results support the hypothesis that APTS effectively protects copper in a 3% NaCl solution by improving the specimen's passive condition and preventing its dissolution in the corrosive environment.
3.2 Adsorption isotherm

Understanding the nature of the interactions occurring at the interface between the inhibitor and the metal and determining the adsorption kinetics of the inhibitor on the metal surface are important goals of the adsorption isotherm (Jorcin et al. 2009). To investigate the adsorption properties of the APTS compound on pure copper in a 3% NaCl solution, we used the following equations to plot the concentration change against the recovery rate, which is represented as $C = f(\theta)$ (Wang et al. 2016; Liao et al. 2016).

$$\frac{C_{\text{inh}}}{\theta} = C_{\text{ads}} + \frac{1}{K_{\text{ads}}}$$  \hspace{1cm} \text{Eqn. 12}

$$K_{\text{ads}} = \frac{1}{55.5} \exp \left( -\frac{\Delta G_{\text{ads}}^0}{RT} \right)$$  \hspace{1cm} \text{Eqn. 13}

The results of this study are shown in Figure 2.

![Figure 2](image)

**Figure 2.** Adsorption of APTS according to the Langmuir isotherm in 3% NaCl at 298 K.

This figure illustrates that the APTS concentration’s change relative to the recovery rate adheres to the Langmuir isotherm. The different values of $\Delta G_{\text{ads}}^0$ make it possible to make a distinction between the various modes of adsorption. When $\Delta G_{\text{ads}}^0$ is less than -40 kJ/mol, the inhibitor is chemically adsorbed on metal. If $\Delta G_{\text{ads}}^0$ is between -40 and -20 kJ/mol, the adsorption of the inhibitor is of mixed nature. Finally, when $\Delta G_{\text{ads}}^0$ exceeds -20 kJ/mol, the adsorption of the inhibitor is of the physisorption type (El Hamdani et al. 2015, Fouda et al. 2016, Alibakhshi et al. 2018). Based on Figure 2, the value of $\Delta G_{\text{ads}}^0$ calculated is of the order of -37.56 kJ/mol. This shows that the APTS inhibitor adsorbs on the copper surface in a mixed manner.

3.3 Electrochemical impedance measurements

To confirm the previous results and explain the phenomenon involved at the copper / solution interface, we employed time-dependent measurements, specifically electrochemical impedance spectroscopy. The outcomes are depicted in Figure 3. Two observable time constants are present in the electrochemical impedance spectra in the 3% NaCl solution following an hour of immersion of pure copper at the corrosion potential. The first is related to the charge transfer that occurs during the breakdown of copper and is seen at high frequencies ($R_t$, $C_d$). The second is connected to a diffusion phenomenon and is detected at low frequencies ($R_D$, $T_D$) (Trachli et al. 2001).
Incorporating the APTS inhibitor at various concentrations into the corrosive environment accentuates a capacitive response, leading to a modification in the electrochemical impedance diagram's characteristics. This change indicates that the interfacial corrosion process has changed. The polarization resistance increases significantly in relation to the inhibitor concentration, as seen by the impedance graphs. However, after modeling a 2RC parallel circuit with the EC-Lab program, a significant discrepancy is found between the experimental data and the generated schematic. As a result, adding a third time constant becomes essential. The allocation of these time constants is as follows:

The dielectric properties of the film produced by the APTS inhibitor, which are further strengthened by the presence of corrosion byproducts and ionic conduction via the film's pores, are linked to a high frequency segment (Rf-Cf). The associated capacitances (1.61, 1.30, 0.69, and 0.47 µF cm⁻²) are remarkably low, supporting the idea that a protective coating forms on the surface of metallic copper (Gabrielli et al. 2006).

In the depths of the pores, a contribution (Rt - Cd) at intermediate frequencies clarifies the charge transfer process occurring at the contact between the electrolyte and the copper surface. When 10⁻³ M APTS is present, the charge transfer resistance value increases with the inhibitor's concentration and shows a 60-fold increase over the control. This demonstrates the product's important role in reducing charge transfer at the contact between copper and the 3% NaCl solution.

For lower frequencies, a linear trend becomes evident at concentrations of 5.10⁻⁴ and 10⁻³ M, with the respective resistance reaching extremely high values. This phenomenon can be attributed to the faradic process (RF, CF). The parameter fitting outcomes for the (RF-CF) and (Rt-Cd) pairs, extracted from the diagrams in Figure 3, are detailed in Table 2. The findings presented in Table 2 demonstrate how the APTS inhibitor protects copper in a 3% NaCl solution. The creation of a rather thick inhibitor coating with low capacitance is the outcome of this impact. Because the RF values are getting closer to infinity, faradic process torque values are not included in the table. This suggests that the presence of corrosion byproducts strengthens the inhibitor coating that has formed on the metal surface, giving it exceptional resilience (Dermaj et al. 2007). The protective efficacy is approximately 98.4% when using the 10⁻³ M concentration, which is the most effective concentration for APTS. The outcomes

Figure 3. Electrochemical impedance spectroscopy plots for copper in a 3% NaCl solution under various APTS concentration, both with and without the inhibitor.
obtained align closely with those acquired through stationary measurements. With and without the APTS inhibitor, Figure 4 shows the electrical circuit equivalents that were taken from the electrochemical impedance diagrams of copper in a 3% NaCl solution.

**Table 2.** The electrochemical characteristics derived from the copper electrochemical impedance plot in a 3% NaCl solution at varying APTS concentrations.

<table>
<thead>
<tr>
<th>[APTS] (M)</th>
<th>R₀ (Ω cm²)</th>
<th>Cᵢ (µF cm⁻²)</th>
<th>Rᵣ (Ω cm²)</th>
<th>Cᵅ (µF cm⁻²)</th>
<th>Rₜ (kΩ cm²)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.24</td>
<td>-----</td>
<td>-----</td>
<td>152</td>
<td>1.21</td>
<td>-----</td>
</tr>
<tr>
<td>5×10⁻⁵</td>
<td>11.34</td>
<td>1.61</td>
<td>1481</td>
<td>22.48</td>
<td>19.85</td>
<td>93.9</td>
</tr>
<tr>
<td>1×10⁻⁴</td>
<td>11.32</td>
<td>1.30</td>
<td>2650</td>
<td>17.01</td>
<td>26.93</td>
<td>95.5</td>
</tr>
<tr>
<td>5×10⁻⁴</td>
<td>11.38</td>
<td>0.69</td>
<td>6127</td>
<td>11.47</td>
<td>50.45</td>
<td>97.6</td>
</tr>
<tr>
<td>1×10⁻³</td>
<td>11.48</td>
<td>0.47</td>
<td>7770</td>
<td>8.10</td>
<td>73.54</td>
<td>98.4</td>
</tr>
</tbody>
</table>

**Figure 4.** Electrical circuit equivalents derived from the electrochemical impedance diagram (a) without inhibitor and (b) with inhibitor.

To evaluate the effect of the inhibitor studied as a function of time, we plotted the evolution of the impedance diagrams without and with 10⁻³ M in APTS in the corrosive solution at different immersion times. The results obtained are illustrated in Figures 5 and 6. The electrochemical impedance curves show a constant appearance at different immersion periods when the APTS inhibitor is not present, suggesting that the corrosion mechanism is stable. These charts illustrate copper's capacitive properties in a 3% NaCl solution, showing a decrease in polarization resistance over an extended immersion period. Its value is around 2170 Ω cm² after one hour of immersion, and it drops to 1500 Ω cm² after 48 hours. This decrease highlights how copper is more vulnerable to the corrosive effects of chloride ions in this hostile environment, which speeds up the pace at which metals corrode.

**Figure 5.** Electrochemical impedance graphs depicting copper behavior in a 3% NaCl solution over various immersion durations.
The influence of the immersion duration on the electrochemical impedance diagrams at the copper/NaCl interface with the inclusion of $10^{-3}$ M APTS.

The electrochemical impedance curves show a regular pattern at different immersion durations in the presence of $10^{-3}$ M APTS, but with a significant increase in polarization resistance. This rise confirms the existence of a solidified and thick inhibitor layer, which gets stronger the longer the immersion period.

### 3.4. DFT and molecular dynamics simulation

#### 3.4.1 Quantum chemical calculations

Frontier molecular orbitals, which encompass the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), play a crucial role in exploring the chemical reactivity of the inhibitor molecule. Thus, we've investigated the connection between the molecular arrangement, electronic configuration, and the inhibitory efficacy of the molecule under examination. Figures 7 and 8 depict the optimized molecular structures, as well as the HOMO and LUMO, of the inhibitor being studied.

![Figure 7. Optimized molecular structures of the APTS inhibitor.](image)

![Figure 8. APTS- HOMO-LUMO orbital distributions of the APTS.](image)
From the Figure 8, we notice that the HOMO electron density is distributed over the ring containing the nitrogen and sulfur atoms in the inhibitor. These specific atoms within the molecule are the primary candidates for electron donation whereas LUMO is highly localized to the phenyl ring in the APTS inhibitor. The APTS inhibitor molecule can adsorb to the metal surface through donor-acceptor interactions involving phenyl ring \( \pi \) electrons, nitrogen atoms, lone pairs of sulfur and nitrogen atoms, as well as the empty orbitals of the copper atoms. Table 3 presents the results of the quantum chemistry calculations linked to the inhibitory effectiveness of the studied molecules.

Table 3. Quantum chemical parameters of the APTS inhibitor calculated in the aqueous phases.

<table>
<thead>
<tr>
<th>Parameters of the APTS</th>
<th>( E_{\text{HOMO}} ) (eV)</th>
<th>( E_{\text{LUMO}} ) (eV)</th>
<th>( \Delta E ) (eV)</th>
<th>( \mu ) (D)</th>
<th>( A ) (eV)</th>
<th>( I ) (eV)</th>
<th>( \chi ) (eV)</th>
<th>( \eta ) (eV)</th>
<th>( \Delta N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>-5.235</td>
<td>-2.159</td>
<td>3.076</td>
<td>1.464</td>
<td>2.159</td>
<td>5.235</td>
<td>3.697</td>
<td>1.538</td>
<td>0.417</td>
</tr>
</tbody>
</table>

The data in the table indicates that the elevated energy level of the HOMO (-5.235 eV) signifies the inhibitor's capacity to supply electrons to the unoccupied d orbital of the metal, while the lower energy level of the LUMO (-2.159 eV) solely reflects its ability to accept electrons from the occupied metal orbital. Moreover, the low energy (\( \Delta E \)) favors the adsorption of inhibitory molecules on the metal surface. This means that the inhibitor is more reactive to accept electrons from the surface of the metal, thereby forming a strong bond between the metal and the inhibitor.

On the other hand, the electronegativity parameter (\( \chi \)) associated with the chemical potential displays a higher value for the APTS, thus demonstrating better inhibition efficiency. The global hardness (\( \eta \)) is equal to \( \Delta E/2 \), and when the global hardness (\( \eta \)) is low it implies more polarizability and higher inhibition efficiency. Softness (\( \sigma \)) parameters are reciprocal to hardness (\( \eta \)). Indeed, a molecule with a higher value of (\( \sigma \)) is likely to behave as a good corrosion inhibitor (Ghailane et al. 2013; Laabaissi et al. 2020). Regarding the number of transferred electrons (\( \Delta N \)) showing inhibitory performance and resulting from electron donation, if the value of \( \Delta N < 3.6 \), the inhibitory efficiency of a molecule increases with the increase electron release capacity at the metal surface. The \( \Delta N \) values for the APTS inhibitor are less than 3.6. This suggests that it is an electron donor, and the copper surface is the acceptor. This ability to receive the electron from the metallic surface increases the efficiency of inhibition.

In general, the dipole moment (\( \mu \)) can divulge information about the polarity of a molecule. Molecules with a higher value of dipole moment have greater adsorption between chemical molecules and a metal surface (Hsissou et al. 2020). In our research, the (\( \mu \)) value is determined to be 1.464 Debye in an aqueous solution, indicating enhanced inhibition efficacy.

Fukui indices allow to analyze the local reactant within a molecule. First, the Fukui indices represent the reactive centers of molecules sensitive to nucleophilic and electrophilic attacks. As a rule of thumb, the atom within the molecule possessing the highest \( f^+ \) value is generally the favored target for nucleophilic attacks, while the atom with the highest \( f^- \) value is typically the preferred site for electrophilic interactions (Saha et al. 2016). The Fukui functions for the APTS inhibitor have been presented in Table 4. According to this table 4, the atoms C2 (0.108), C6 (0.074), N7 (0.098), C(8)(0.086) and S(12) (0.086) presented the highest values of \( f^+ \) concerning the most sensitive site for nucleophilic attacks, while N11 (0.064) and S12 (0.482) are the preferred sites for electrophilic attacks. Based on these results, the distribution of active sites shows significant differences. This implies the greater adsorption capacity of the APTS inhibitor on the copper surface, validating the significant experimental inhibition effectiveness achieved.
### Table 4. Fukui indices for electrophilic and nucleophilic of the APTS inhibitor.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$f^+$</th>
<th>$f^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>0.030</td>
<td>0.008</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.108</td>
<td>0.023</td>
</tr>
<tr>
<td>C(3)</td>
<td>0.038</td>
<td>0.010</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.062</td>
<td>0.016</td>
</tr>
<tr>
<td>C(5)</td>
<td>0.061</td>
<td>0.006</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.074</td>
<td>0.016</td>
</tr>
<tr>
<td>N(7)</td>
<td>0.098</td>
<td>0.082</td>
</tr>
<tr>
<td>C(8)</td>
<td>0.086</td>
<td>0.056</td>
</tr>
<tr>
<td>N(9)</td>
<td>0.013</td>
<td>0.025</td>
</tr>
<tr>
<td>C(10)</td>
<td>0.011</td>
<td>0.020</td>
</tr>
<tr>
<td>N(11)</td>
<td>0.029</td>
<td>0.064</td>
</tr>
<tr>
<td>S(12)</td>
<td>0.086</td>
<td>0.482</td>
</tr>
<tr>
<td>H(13)</td>
<td>0.024</td>
<td>0.035</td>
</tr>
<tr>
<td>N(14)</td>
<td>0.010</td>
<td>0.023</td>
</tr>
<tr>
<td>H(15)</td>
<td>0.019</td>
<td>0.024</td>
</tr>
<tr>
<td>H(16)</td>
<td>0.015</td>
<td>0.035</td>
</tr>
<tr>
<td>H(17)</td>
<td>0.046</td>
<td>0.017</td>
</tr>
<tr>
<td>H(18)</td>
<td>0.044</td>
<td>0.012</td>
</tr>
<tr>
<td>H(19)</td>
<td>0.053</td>
<td>0.014</td>
</tr>
<tr>
<td>H(20)</td>
<td>0.043</td>
<td>0.012</td>
</tr>
<tr>
<td>H(21)</td>
<td>0.051</td>
<td>0.019</td>
</tr>
</tbody>
</table>

#### 3.4.2 APTS inhibitory effect study on Cu (110) in NaCl solution

The adsorption energy ($E_{\text{adsorption}}$) pertaining to the inhibitors presence on the surface of Cu(111) was obtained using the following equation (Dutta et al. 2015):

\[
E_{\text{adsorption}} = E_{\text{system}} - (E_{\text{surface+solution}} + E_{\text{inhibitor+solution}}) + E_{\text{solution}}
\]

**Eqn. 14**

In this equation, $E_{\text{total}}$ signifies the overall energy of the entire system, $E_{\text{surface+solution}}$ accounts for the combined energy of the surface and the Cu(110) solution in the absence of the APTS inhibitor, $E_{\text{inhibitor+solution}}$ represents the cumulative energy of the APTS inhibitor and the solution, and $E_{\text{solution}}$ is indicative of the total energy contributed by the (3Na$^+$, 3Cl$^-$, and 200 H$_2$O) entities. The binding energy corresponds to the negative value of the adsorption energy. It is given as follows:

\[
E_{\text{adsorption}} = -E_{\text{binding}}
\]

**Eqn. 15**

The equilibrium adsorption configuration of the inhibitor molecule obtained in aqueous solution from the forcite module is shown in Figure 9.

**Figure 9** illustrates the robust interaction of the APTS inhibitor with the metal surface, resulting in its flat adsorption. This phenomenon can be attributed to a donor-acceptor interaction between the inhibitory molecules and the metal surface. The APTS inhibitor's structure features N and S donor heteroatoms as well as $\pi$ electrons, enabling it to supply numerous electrons to the vacant d orbitals of copper. Furthermore, the antibonding $\pi$-orbitals of the phenyl ring exhibit a considerable ability to accept electrons from the 4s or 3d orbitals of copper, forming coordinated bonds. This parallel alignment is a prevalent feature in numerous large organic corrosion inhibitors (Shi et al. 2012, Murmu et al. 2019), where p-d hybridization assumes a pivotal role.
**Figure 9.** Equilibrium adsorption patterns of the inhibitor on the Cu(111) surface; (A) side view (B) front view

**Table 5.** Adsorption energy values between the APTS inhibitor and the Cu(111) surface.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>( E_{\text{systeme}} ) (kcal/mol)</th>
<th>( E_{\text{surface+solution}} ) (kcal/mol)</th>
<th>( E_{\text{inhibitor+solution}} ) (kcal/mol)</th>
<th>( E_{\text{solution}} ) (kcal/mol)</th>
<th>( E_{\text{ads}} ) (kcal/mol)</th>
<th>( E_{\text{binding}} ) (kcal/mol)</th>
</tr>
</thead>
</table>

**Table 6.** Distance between some atoms of the inhibitor and the atom closest to the surface of Cu (111)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Distance(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N7/Cu</td>
<td>3.667</td>
</tr>
<tr>
<td>N9/Cu</td>
<td>3.4121</td>
</tr>
<tr>
<td>N14/Cu</td>
<td>2.826</td>
</tr>
<tr>
<td>S12/Cu</td>
<td>2.989</td>
</tr>
<tr>
<td>Cl/Cu</td>
<td>3.139</td>
</tr>
<tr>
<td>C2/Cu</td>
<td>3.353</td>
</tr>
<tr>
<td>C3/Cu</td>
<td>3.108</td>
</tr>
<tr>
<td>C4/Cu</td>
<td>3.194</td>
</tr>
<tr>
<td>C5/Cu</td>
<td>2.929</td>
</tr>
<tr>
<td>C6/Cu</td>
<td>3.349</td>
</tr>
</tbody>
</table>

We looked at the effects of electrostatic interactions between Cu atoms on the Cu(111) surface and N and S, the inhibitor's most electronegative centers, in order to improve this adsorption. We determined the closest bond distance between the interacting heteroatom and the closest metal surface atom, as indicated in **Table 6**. In general, a strong chemical interaction between the interacting atoms of the inhibitor molecule and the metal surface atoms is indicated by a bond distance of less than 3.5 Å. On the other hand, a bond distance greater than 3.5 Å indicates a Van der Waals-type contact between the involved atoms (Zeng et al. 2011). The data in **Table 6** demonstrates that the inhibitor molecules' heteroatoms and the surface's copper atoms are the closest in distance, both less than 3.5 Å. This result confirms that the inhibitor molecule's heteroatoms and the surface's copper atoms have formed chemical linkages that aid in the APTS inhibitor molecule's adsorption.

A molecular dynamics (MD) simulation was performed to determine the interaction energy and binding energy associated with the interaction between inhibitor molecules and the Cu(111) surface in order to evaluate the inhibitor molecule's adsorption capacity. -502.2964 (kcal/mol) is the interaction energy value for the inhibitor (**Table 5**). The considerable negative energy values signify the inhibitor molecule's spontaneous and robust adsorption onto the copper surface (Madkour et al. 2016; Zhou et al., 2015). Furthermore, by examining the binding energy values, the effectiveness of inhibitor adsorption on this surface may be determined. Greater binding energy values indicate better adsorption properties. The binding energy values for the inhibitory compounds are -502.2964 (kcal/mol), according to the data (**Table 5**). In fact, increased inhibition efficacy is correlated with an inhibitor's better adsorption capacity.
Conclusion

The study of the inhibitory effect of APTS against copper corrosion in an aggressive 3% NaCl solution by potentiodynamic polarization tests unveiled that this compound is a mixed inhibitor which acts in low concentration. Its effect is characterized by a strong reduction in both the cathodic and anodic currents and a shift in the corrosion potential towards the positive direction. In the anodic range and for the 5x10^{-4} M and 10^{-3} M concentrations, there appears a pseudo current level of low value reflecting the formation of a protective film on the copper's metal surface. Electrochemical impedance measurements revealed that introducing the APTS inhibitor at various concentrations led to the emergence of a capacitive loop at high frequencies, characterized by low capacitance. This observation is linked to the development of an inhibitor film, bolstered by the presence of corrosion by products. This reinforces the passive state of the copper in the corrosive solution. The preventive effect of APTS is justified by the inhibitory efficiency, which is almost 98%. The theoretical analysis of this substance validates its attachment to the copper's metallic surface, generating a protective layer. This substantiates the assumption made in the experimental study regarding the inhibitor film's formation.

Disclosure statement: Conflict of Interest: The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

References


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