Corrosion inhibition of aluminum-silicon alloy in H$_2$SO$_4$ solution using some thiophene derivatives

Inhibition of corrosion of Al-Si alloy by some thiophene derivatives in 0.5M H$_2$SO$_4$ was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Polarization studies were carried out at different temperatures and showed that the investigated compounds are anodic inhibitors. The effect of temperature on corrosion inhibition has been studied and thermodynamic activation and adsorption parameters were calculated and discussed. Electrochemical impedance was used to investigate the mechanism of corrosion inhibition. The inhibition occurs through adsorption of the investigated compounds on the alloy surface without modifying the mechanism of corrosion process. The experimental data fit both of Temkin and kinetic-thermodynamic isotherm. A clear correlation was found between corrosion inhibition efficiency and theoretical parameters obtained by PM3 semiempirical method. The experimental results are supported by the theoretical data.

Keywords: Thiophene derivatives; corrosion inhibition; Al-Si alloy; H$_2$SO$_4$, quantum chemical calculations.

1. INTRODUCTION

Aluminum and its alloys are widely used because of their appearance, low density and corrosion resistance. Nevertheless sometimes additional protection is required. Then, aluminum alloys can be easily protected with organic coatings by electrochemical oxidation. The latter generates oxide passive layers providing excellent corrosion resistance in highly aggressive environments. However, due to different thermomechanical treatments applied to achieve the mechanical properties, they are liable to suffer from various forms of corrosion, mainly pitting and intregranular attack [1-2]. Aluminum alloys are important structural metals, particularly in the aerospace industry. Pure aluminum metal (without alloying elements) is rather corrosion resistant, a result of passive film that forms on the metal surface. However, pure aluminum metal does not posses adequate strength for most aerospace application and must be alloyed with other metals, notably copper, magnesium, silicon, iron, zinc and other minor constituent. These alloys are classified by a numbering system that reflects both the chemical composition and the heat treatment (tempering) of the alloy [3-4]. The use of organic compounds as corrosion inhibitors for Al and Al alloys in HCl and H$_2$SO$_4$ acids have been the object of large number of investigators [5-18].

The present work was designed to study the corrosion inhibition of Al-Si alloy in H$_2$SO$_4$ solutions by some thiophene derivatives as corrosion inhibitors using different techniques. The synergistic effect brought about by combination of the inhibitors with LaCl$_3$ was examined also and explained.

2. MATERIALS AND METHODS

2.1. Materials and solutions

The aluminum-silicon alloy which employed for this study has a composition 89.15% Al and 10.85% Si. A cylindrical alloy rod whose exposed surface was 1 cm$^2$ was inserted into a Teflon tube so that only the flat surface was in contact with solution. Before each experiment, the electrode was abraded with a sequence of emery papers of different grades (600, 800, 1200), washed with double distilled water and degreased with acetone. All chemicals used were of analytical-grade reagents. Solutions were prepared using double distilled water. The corrosive solution was 0.5 M sulfuric acid and prepared using double distilled water. The experiments were carried out under non-stirred and naturally aerated conditions. The inhibitor solutions were prepared at different concentrations using absolute ethanol.

2.2 Inhibitors

The selected organic inhibitors used in this study were synthesized through procedures reported previously [19]. The structure formulae of inhibitors are shown in Fig. 1.

![Fig. 1 - Potentiodynamic curves for the Al-Si alloy in 0.5M of H$_2$SO$_4$ in the presence and absence of different concentrations of compound A at 25°C](image-url)
2.2 Methods

2.2.1. Potentiodynamic polarization

Electrochemical experiments were performed in a conventional three-electrode electrochemical cell at 25 °C with a platinum counter electrode and saturated calomel (SCE) as reference electrode. The working electrode was in the form of a disc cut from the alloy under investigation, first was immersed into the test solution for 30 min to establish a steady state open circuit potential.

The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -250 mV to +250 mV with a scanning rate of 5 mV s⁻¹ using Gamry framework instruments (version 3.20). Corrosion current densities (j_{corr}) and corrosion potential (E_{corr}), where evaluated from intersection of the linear anodic and cathodic branches of Tafel plots and all of them will calculated in absence and presence of different concentrations of inhibitors. Experiments were always repeated at least three times. Degree of surface coverage (θ) is calculated, as proposed by Vracar and Drazie [20], from the following equation:

\[ \theta = \frac{(j_{corr} - j'_{corr})/j_{corr}} \]

\[ \% \text{IE} = \theta \times 100 \]

where R’ct and R_{ct} are the charge transfer resistance in the presence and absence of inhibitor, respectively.

2.2.2. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy were performed at corrosion potentials, E_{corr}, over a frequency range of 10⁻² Hz to 0.5 Hz with a signal amplitude perturbation of 10 mV, using potentiostat /galvanostat (Gamry PCI 300/4) and personal computer with EIS300 software for calculations. Data were presented as Nyquist and Bode plots. Experiments were always repeated at least three times. Degree of surface coverage (θ) and % IE were calculated using the following equations:

\[ \theta = \frac{(1/R'_{ct})-(1/R_{ct})/(1/R'_{ct})} \]

\[ \% \text{IE} = \theta \times 100 \]

where R’ct and R_{ct} are the charge transfer resistance in the presence and absence of inhibitor, respectively.

2.3. Quantum calculations

Materials studio V.4.4.0 was used for molecular modeling. The molecular orbital calculation are based on a semicircular self-consistent field molecular orbital (SCF-MO) method. A full optimization of all geometrical variables without any symmetry constraints was performed at the restricted Hartree–Fock (RHF) level using Parameterization Model 3 (PM3) method.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization measurements

Figure (1) shows both the cathodic and anodic polarization curves of Al-Si alloy in the presence and absence of different concentrations of compound (C). Similar curves were obtained for the other compounds (not shown). Table (1) shows the electrochemical parameters of corrosion potential (E_{corr}), corrosion current densities (j_{corr}), cathodic and anodic Tafel slopes (β_c & β_a), the degree of surface coverage (θ), and % IE were calculated using the following equations:

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Structure</th>
<th>Mol. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>2-amino-5,6-dihydro-4H-cyclopenta[b]thiophene -3-carboxylic acid</td>
<td></td>
<td>183</td>
</tr>
<tr>
<td>(B)</td>
<td>2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene -3-carboxylic acid</td>
<td></td>
<td>197</td>
</tr>
<tr>
<td>(C)</td>
<td>2-amino-5,6,7,8-tetrahydro-4H-cyclohepta[b]thiophene -3-carboxylic acid</td>
<td></td>
<td>211</td>
</tr>
</tbody>
</table>

The data show that the corrosion current density (j_{corr}) decreases with increasing the concentration of inhibitors. The order of decreasing the values of (j_{corr}) and hence the rate of corrosion is as follows: A > B > C. The slopes of the anodic (β_a) and cathodic (β_c) Tafel lines remain almost constant upon increasing inhibitor concentrations. These results indicate that these inhibitors act by blocking the available surface area [21]. In other words, these inhibitors decrease the surface area for corrosion without affecting the mechanism of corrosion and only cause inactivation of a part of metal surface with respect to the
corrosive medium. The slight shift of corrosion potential ($E_{corr}$) values towards less negative direction by increase of the inhibitor concentrations in the presence of 0.5 M H$_2$SO$_4$ indicates that these investigated compounds are anodic inhibitors [22].

Table 1 - The effect of concentration of the investigated compounds on the free corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), Tafel slopes ($\beta_a$ & $\beta_c$), inhibition efficiency (% IE), degree of surface coverage ($\theta$) and corrosion rate (CR) for the corrosion of Al-Si alloy in H$_2$SO$_4$ at 25°C

<table>
<thead>
<tr>
<th>compounds</th>
<th>Conc. µm M</th>
<th>$E_{corr}$ mV</th>
<th>$i_{corr}$ µA cm$^{-2}$</th>
<th>$\beta_a$ mVdec$^{-1}$</th>
<th>$\beta_c$ mVdec$^{-1}$</th>
<th>$\theta$</th>
<th>% IE</th>
<th>CR mm y$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free acid</td>
<td>0.0</td>
<td>732</td>
<td>161.9</td>
<td>179</td>
<td>466</td>
<td>----</td>
<td>----</td>
<td>1.795</td>
</tr>
<tr>
<td>(A)</td>
<td>1</td>
<td>697</td>
<td>94.88</td>
<td>186</td>
<td>366</td>
<td>0.413</td>
<td>41.3</td>
<td>1.031</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>685</td>
<td>82.26</td>
<td>217</td>
<td>429</td>
<td>0.492</td>
<td>49.2</td>
<td>0.894</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>664</td>
<td>56.70</td>
<td>201</td>
<td>375</td>
<td>0.650</td>
<td>65.0</td>
<td>0.616</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>677</td>
<td>39.81</td>
<td>170</td>
<td>282</td>
<td>0.754</td>
<td>75.4</td>
<td>0.433</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>652</td>
<td>31.77</td>
<td>181</td>
<td>327</td>
<td>0.804</td>
<td>80.4</td>
<td>0.345</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>640</td>
<td>28.23</td>
<td>192</td>
<td>320</td>
<td>0.826</td>
<td>82.6</td>
<td>0.307</td>
</tr>
<tr>
<td>(B)</td>
<td>1</td>
<td>707</td>
<td>118.9</td>
<td>123</td>
<td>525</td>
<td>0.271</td>
<td>27.1</td>
<td>1.292</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>690</td>
<td>104.7</td>
<td>222</td>
<td>546</td>
<td>0.353</td>
<td>35.3</td>
<td>1.138</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>644</td>
<td>67.65</td>
<td>212</td>
<td>414</td>
<td>0.582</td>
<td>58.2</td>
<td>0.735</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>674</td>
<td>49.66</td>
<td>200</td>
<td>359</td>
<td>0.693</td>
<td>69.3</td>
<td>0.540</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>642</td>
<td>32.53</td>
<td>188</td>
<td>308</td>
<td>0.799</td>
<td>79.9</td>
<td>0.353</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>646</td>
<td>29.91</td>
<td>191</td>
<td>296</td>
<td>0.815</td>
<td>81.5</td>
<td>0.325</td>
</tr>
<tr>
<td>(C)</td>
<td>1</td>
<td>749</td>
<td>147.3</td>
<td>181</td>
<td>461</td>
<td>0.090</td>
<td>9.0</td>
<td>1.600</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>744</td>
<td>110.8</td>
<td>164</td>
<td>351</td>
<td>0.315</td>
<td>31.5</td>
<td>1.204</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>751</td>
<td>99.25</td>
<td>179</td>
<td>387</td>
<td>0.387</td>
<td>38.7</td>
<td>1.079</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>761</td>
<td>74.83</td>
<td>157</td>
<td>313</td>
<td>0.538</td>
<td>53.8</td>
<td>0.813</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>672</td>
<td>50.54</td>
<td>195</td>
<td>333</td>
<td>0.688</td>
<td>68.8</td>
<td>0.549</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>655</td>
<td>39.64</td>
<td>187</td>
<td>308</td>
<td>0.755</td>
<td>75.5</td>
<td>0.431</td>
</tr>
</tbody>
</table>

From the calculated values of (% IE) at 25 °C as shown in Table 2, the order of decreasing the inhibition efficiency of the investigated compounds is as follows: A > B > C

Table 2 - Inhibition efficiency at different concentration of the investigated compounds for the corrosion of Al-Si alloy in 0.5M H$_2$SO$_4$ at 25°C

<table>
<thead>
<tr>
<th>Concentration, µm M</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.3</td>
<td>27.1</td>
<td>9.0</td>
</tr>
<tr>
<td>3</td>
<td>49.2</td>
<td>35.3</td>
<td>31.5</td>
</tr>
<tr>
<td>5</td>
<td>65.0</td>
<td>58.2</td>
<td>38.7</td>
</tr>
<tr>
<td>7</td>
<td>75.4</td>
<td>69.3</td>
<td>53.8</td>
</tr>
<tr>
<td>9</td>
<td>80.4</td>
<td>79.9</td>
<td>68.8</td>
</tr>
<tr>
<td>11</td>
<td>82.6</td>
<td>81.5</td>
<td>75.5</td>
</tr>
</tbody>
</table>

3.2 Electrochemical impedance spectroscopy

The corrosion behavior of Al-Si alloy in 0.5 M H$_2$SO$_4$ in the presence and absence of investigated thiophene derivatives was investigated by (EIS) at 25 °C. Various impedance parameter such as charge transfer resistance ($R_{ct}$), double layer capacitance ($C_{dl}$) and inhibition efficiency (% IE) were calculated and are given in Table 3. The data obtained show that ($R_{ct}$) charge transfer resistance increases with increasing the concentration of inhibitors which accompanied with increasing (% IE) and the value of capacitance double layer ($C_{dl}$) decrease with increasing the concentration of inhibitor due to the adsorption of these compound on the electrode surface leading to a film formation of Al-Si alloy surface.
Table 3 - Electrochemical kinetic parameter obtained by EIS technique for the corrosion of Al-Si alloy in 0.5M H₂SO₄ at different concentration of investigated compound.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Concentration µM</th>
<th>C_d, µF cm⁻²</th>
<th>R_p, Ω cm²</th>
<th>Θ</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>0.0</td>
<td>27.91</td>
<td>122.9</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>A</td>
<td>5</td>
<td>24.72</td>
<td>160.9</td>
<td>0.236</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>20.26</td>
<td>179.4</td>
<td>0.315</td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>16.52</td>
<td>202.8</td>
<td>0.394</td>
<td>39.4</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>6.348</td>
<td>237.3</td>
<td>0.482</td>
<td>48.2</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>25.31</td>
<td>155.1</td>
<td>0.208</td>
<td>20.8</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>21.02</td>
<td>174.3</td>
<td>0.295</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>14.11</td>
<td>199.2</td>
<td>0.383</td>
<td>38.3</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>8.09</td>
<td>226.5</td>
<td>0.457</td>
<td>45.8</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>24.96</td>
<td>149.9</td>
<td>0.180</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>23.35</td>
<td>165.0</td>
<td>0.255</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>17.42</td>
<td>178.9</td>
<td>0.314</td>
<td>31.4</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>11.52</td>
<td>211.7</td>
<td>0.42</td>
<td>42.0</td>
</tr>
</tbody>
</table>

The obtained Nyquist impedance diagram in most cases does not show perfect semicircle. This may be attributed to the frequency dispersion as a result of the heterogeneity of the electrode surface [23-24].

In 0.5 M H₂SO₄ and presence of various concentrations of investigated inhibitors, the impedance diagram shows the same trend. However, the diameters of the capacitative loop increase with increasing concentration of the inhibitor. Fig (2) shows the Nyquist plot for Al-Si alloy in 0.5 M H₂SO₄ in the absence and presence of different concentrations of compound (A) at 25 °C.

This diagram has a semicircle appearance; it indicates that the corrosion of Al-Si alloy is mainly controlled by a charge transfer process. The Bode plot for the alloy is shown in Figure (3) where the high frequency limit corresponds to electrolyte resistance Rₑ, while the low frequency limit represents the sum of (Rₑ + R_p) where R_p is the first approximation determined by both the electrolytic conductance of the oxide film and polarization resistance of the dissolution and repassivation process.

![Fig. 2](image1.png)  
**Fig. 2** - The Nyquist plot for Al-Si alloy in 0.5 M H₂SO₄ solution in the absence and presence of different concentration of compound (A) at 25 °C

![Fig. 3](image2.png)  
**Fig. 3** - The Bode plot for Al-Si alloy in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations of compound (A) at 25 °C
3.3 Adsorption isotherm

The investigated compounds inhibit the corrosion by adsorption at the metal surface. Theoretically, the adsorption process has been regarded as a simple substitutional process, in which an organic molecule in the aqueous phase substitutes an \( y \) number of water molecules adsorbed on the metal surface [25].

A number of mathematical relationships for the adsorption isotherms have been suggested to fit the experimental data of the present work. The simplest equation is that due to Temkin [26] and is given by the general relation:

\[
a \Theta = KC \tag{5}
\]

where \( K \) is the equilibrium constant of the adsorption reaction, \( C \) is the inhibitor concentration in the bulk of the solution.

According to Temkin model, the data (Table 4) indicate that the value of \( K \) decreases in the order: \( A > B > C \). It is seen that there is a good agreement between the values of \( K \) and \( \Delta G^\text{ads} \) obtained from the kinetic model and Temkin model isotherm.

\[
\begin{array}{|c|c|c|}
\hline
\text{Inhibitor} & K \times 10^{-4} \text{ M}^{-1} & -\Delta G^\text{ads} \text{ kJ mol}^{-1} \\
\hline
A & 1.18 & 42.48 \\
B & 0.90 & 41.27 \\
C & 0.72 & 39.93 \\
\hline
\end{array}
\]

According to Temkin model, the data (Table 4) indicate that the value of \( K \) decreases in the order: \( A > B > C \). It is seen that there is a good agreement between the values of \( K \) and \( \Delta G^\text{ads} \) obtained from the kinetic model and Temkin model isotherm.

\[
\begin{array}{|c|c|c|}
\hline
\text{Inhibitor} & K \times 10^{-4} \text{ M}^{-1} & -\Delta G^\text{ads} \text{ kJ mol}^{-1} \\
\hline
A & 686.12 & 48.96 \\
B & 220.90 & 46.15 \\
C & 100.88 & 44.21 \\
\hline
\end{array}
\]
3.4 Effect of temperature

Temperature has a significant influence on metals and alloys corrosion rates. In case of corrosion in an acidic medium, the corrosion rate increases with increase in temperature, because the decrease of hydrogen evolution overpotential [5]. An experimental dependence of Arrhenius-type equation on temperature is observed between the corrosion rate and temperature.

\[ j_{\text{corr}} = A \exp(-E_a/RT) \quad (8) \]

and logarithmic form

\[ \log j_{\text{corr}} = \log A \left(-E_a/2.303RT\right) \quad (9) \]

where \( j_{\text{corr}} \) is the corrosion current density, \( A \) is the extrapolation factor, \( E_a \) is the activation energy, \( R \) is the gas constant and \( T \) is the absolute temperature.

The effect of rising temperature on the corrosion rate of Al-Si alloy in 0.5 M H\(_2\)SO\(_4\) solution in the absence and presence of 3x10\(^{-6}\) M of the investigated thiophene derivatives was studied by potentiodynamic polarization over a temperature range from 25-40 °C. Corrosion rates in all systems increased to a great extent as temperature was raised from 25°C to 40°C. Also, investigated compounds are seen to maintain their inhibiting effect at all temperatures. The above observations can be explained with respect to the characteristic features of the cathodic process of hydrogen evolution, where the decrease of the reaction overpotential with rise in temperature leads to an increase in the rate of cathodic reaction [28]. The enhanced rates of hydrogen gas evolution will agitate the interface, which hinders inhibitor adsorption and also promotes dispersal of adsorbed inhibitor. Thus, the reduction in % IE with rise in temperature could be attributed to the shift of the adsorption-desorption equilibrium towards desorption. Such behavior suggests that investigated compounds were physically adsorbed on Al-Si alloy [29].

Relation between log (rate) and reciprocal of the absolute temperature of Al-Si alloy in 0.5 M H\(_2\)SO\(_4\) in the presence and absence of investigated compounds. The values of \( E_a \) are given in Table (5). Data of this Table reveal high activation energies for the inhibition process by different compounds, indicating their higher protective efficiency [22]. It is clear that the activation energy increases with increasing the efficiency of the investigated compounds in the following order: C < B < A. Such behavior is attributed to the formation of energy barrier, due to the adsorption of the inhibitors on the alloy surface forming a film. This is another pointer to inhibitor physisorption.

Table 5 - Thermodynamic activation parameters for Al-Si alloy dissolution in 0.5 M H\(_2\)SO\(_4\) in absence and presence of 3x10\(^{-6}\) M of investigated inhibitors.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>( E_a ) kJ mol(^{-1})</th>
<th>( H^\Delta ) kJ mol(^{-1})</th>
<th>( S^\Delta - \Delta ) J mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>66.3</td>
<td>63.8</td>
<td>101</td>
</tr>
<tr>
<td>A</td>
<td>86.9</td>
<td>76.2</td>
<td>64</td>
</tr>
<tr>
<td>B</td>
<td>78.2</td>
<td>75.9</td>
<td>66</td>
</tr>
<tr>
<td>C</td>
<td>75.3</td>
<td>72.8</td>
<td>74.7</td>
</tr>
</tbody>
</table>

An alternative formulation of arhenius equation is the transition state equation [30].

\[ j_{\text{corr}} = RT/Nh \exp \left(\Delta S^*/R\right)\exp\left(-\Delta H^*/RT\right) \quad (10) \]

where \( h \) is the Planck’s constant, \( N \) is Avogadro number, \( \Delta S^* \) is the entropy change of activation and \( \Delta H^* \) is the enthalpy change of activation. Figure (7) shows a plot of log (\( j_{\text{corr}}/T \)) against (1/T) straight line are obtained with a slope of \( (-\Delta H^*/2.303R) \) and intercept of (log \( R/Nh + \Delta S^*/2.303R \)) from which the value of \( \Delta H^* \) & \( \Delta S^* \) are calculated and are given in Table (5).

Fig. 6 - Arrhenius plots (log \( j_{\text{corr}} \) vs. 1/ T) for Al-Si alloy in 0.5 M H\(_2\)SO\(_4\) in the absence and presence of 3 \( \mu \)M of investigated inhibitors

A plot of (log \( j_{\text{corr}} \) vs. 1/T) gives straight lines with slope \( E_a/2.303R \). The intercept be A. Fig.6 represents the relation between log (rate) and reciprocal of the absolute temperature of Al-Si alloy in 0.5 M H\(_2\)SO\(_4\) in the presence and absence of investigated compounds. The values of \( E_a \) are given in Table (5). Data of this Table reveal high activation energies for the inhibition process by different compounds, indicating their higher protective efficiency [22]. It is clear that the activation energy increases with increasing the efficiency of the investigated compounds in the following order: C < B < A. Such behavior is attributed to the formation of energy barrier, due to the adsorption of the inhibitors on the alloy surface forming a film. This is another pointer to inhibitor physisorption.

Fig. 7 - Arrhenius plots log \( j_{\text{corr}}/ T \) vs. (1/ T) for Al-Si alloy in 0.5 M H\(_2\)SO\(_4\) in the absence and presence of 3 \( \mu \)M of investigated inhibitors.
From Table (5) it is clear that the positive value of \( \Delta H^* \) reflects the endothermic nature of dissolution process. The Table also shows that the presence of the inhibitor produces higher values for \( \Delta H^* \) than those obtained for the uninhibited solution. This indicates higher protection efficiency. This may be attributed to the presence of an energy barrier for the reaction, that is, the process of adsorption leads to a rise in enthalpy of the corrosion process. In addition, the values of \( \Delta S^* \) are large and negative. This implies that the activated complex in the rate determining step represents association rather than dissociation meaning that a decrease in disordering takes place on going from reactants to activated complex and the increase in the system order [31, 32].

### 3.5 Theoretical studies

To investigate the effect of ring structure on the inhibition mechanism and efficiency some quantum chemical calculations were performed.

Geometric and electronic structures of the inhibitors were calculated by optimization of their bond lengths and bond angles. The optimized molecular structures of the inhibitors are given in Fig.8b. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, LUMO-HOMO energy gap, dipole moment, \( \mu \), and inhibition efficiency are given in Table 6.

#### Table 6 - Quantum chemical parameter for investigated thiophene derivatives

<table>
<thead>
<tr>
<th>Comp.</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9.704</td>
<td>0.743</td>
</tr>
<tr>
<td>B</td>
<td>8.957</td>
<td>0.825</td>
</tr>
<tr>
<td>C</td>
<td>8.801</td>
<td>0.565</td>
</tr>
</tbody>
</table>

\( E_{\text{HOMO}} \) often is associated with the electron donating ability of the molecule. High values of \( E_{\text{HOMO}} \) are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbitals. Therefore, the energy of the lowest unoccupied molecular orbitals indicates the ability of the molecule to accept electrons. The lower the value of \( E_{\text{LUMO}} \), the most probable it is that the molecule accepts electron [33]. The percent inhibition efficiencies increase if the molecules have higher or less negative HOMO energies. The highest values of the HOMO density were found in the vicinity of sulphur and nitrogen atoms, clearly indicating the nucleophilic center is the sulphur and nitrogen atoms (Fig. 8a).
Table 6 shows the calculated values of dipole moment, $\mu$, of the studied molecules. Highest dipole moment values were observed with compound (A). Other authors state that the inhibition efficiency increases with increasing value of the dipole moment [34] but on the other hand, a survey of literature reveals that irregularities appeared in the case of correlation of dipole moment with efficiency [35]. Also, from this Table the value of $\Delta E$ (energy gap) decreased when increasing the inhibition efficiency indicating that the more of inhibitors, the stronger interaction between inhibitors and metal surface. Thus, the interactions are probably physical adsorption, and the interactions between the inhibitors and the metal surface might be ascribed to the hyper conjugation interactions-$\pi$ stacking [36].

As gathered from the higher values of $E_{\text{HOMO}}$, dipole moment and the lower values of $E_{\text{LUMO}}$ the order on inhibition efficiency is as follows: $A > B > C$.

3.6. Mechanism of corrosion inhibition

Corrosion inhibition of aluminum-silicon alloy in $\text{H}_2\text{SO}_4$ solution by the investigated thiophene derivatives as indicated from potentiodynamic and impedance techniques was found to depend on the concentration and the nature of the inhibitor.

It is generally, assumed that adsorption of the inhibitor at the metal / solution interface is the first step in the action mechanism of the inhibitors in aggressive acid media. Four types of adsorption may take place during inhibition involving organic molecules at the metal / solution interface:
1) Electrostatic attraction between charged molecules and charged metal.
2) Interaction of unshared electrons pairs in the molecule with the metal.
3) Interaction of $\pi$ electrons with the metal.
4) A combination of the above [37].

Concerning inhibitors, the inhibition efficiency depends on several factors; such as: (i) the number of adsorption sites and their charge density, (ii) molecular size, heat of hydrogenation, (iii) mode of interaction with the metal surface, and (iv) the formation metallic complexes [38]. Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulfur or oxygen, each of them in principle representing an adsorption center. The inhibitive properties of such compounds depend on the electron densities surrounding the adsorption centers: the higher the electron density at the center, the more the effective the inhibitor.

In the aqueous acidic solutions, investigated compounds exist either as neutral molecules or in the form of cations (protonated). In general two modes of adsorption could be considered. The neutral form may adsorb on the alloy surface via the chemisorption mechanism, involving the displacement of water molecules from the metal surface and the sharing electrons between the N, O, and S atoms and Al. The cationic form can also adsorb on the metal surface on the basis of donor-acceptor interactions between $\pi$-electrons of aromatic ring and vacant $p$-orbitals of Al. On the other hand, it is well known that the Al surface charges negative charge in acid solution [39, 40], so, the protonated investigated compounds may adsorb through electrostatic interactions between positively charged molecules and the negatively charged metal surface. When the protonated form is adsorbed on the metal surface, a coordinate bond may be formed by partial transference of electrons from N, O, and S atoms to the metal surface. In addition, owing to lone-pair electrons of N, O, and S atoms in the investigated compounds or the protonated form may combine with freshly generated Al$^{3+}$ ions on Al surface forming metal inhibitor complexes. These complexes might get adsorbed onto Al surface by van der Waals force to form protective film which covers both anodic and cathodic reaction sites on the Al surface, and inhibits both reactions at the same time.

In the investigated thiophene derivatives the effective part in these molecules is the cyclopentane, cyclohexane and cycloheptane. As known from the stereochemistry of these cycloalkanes the cyclopentane was found to lie flat completely on the alloy surface so, it covers larger areas of alloy surface than in case of cyclohexane and cycloheptane which are partially lie flat on the alloy surface. So, the inhibition efficiency of the investigated thiophene derivatives is as follows: $A>B>C$.

4. CONCLUSIONS

From the study the following conclusions can be made:

i. Thiophene derivatives are good inhibitors of corrosion of Al-Si alloy in $\text{H}_2\text{SO}_4$ and inhibit the corrosion by being adsorbed onto the alloy surface.

ii. The adsorption behavior of the inhibitors is consistent with Temkin adsorption model.

iii. The mechanism of physical adsorption is applicable to the adsorption of the investigated thiophene derivatives on surface of Al-Si alloy.

vi. The results of polarization indicated that these investigated compounds are of anodic inhibitors.

v. As can seen, good agreement between potentiodynamic polarization measurements, electrochemical impedance measurements and quantum chemical calculations is found.

5. REFERENCES


