Corrosion inhibitory studies of an eco-friendly thiourea derivative of amino acid on aluminium using 0.1M HCl solution

Fayomi Omotola Michael 1, *, Akande James Asamu 2, Olayemi Ifeoluwa Oluwatosin 2 and Kalu Chidiebere Raphael 1

1 Department of Chemistry, Joseph Sarwuan Tarka University, Makurdi. Nigeria.
2 Department of Chemistry and Biochemistry, Caleb University, Imota, Lagos. Nigeria.

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Abstract
The inhibition efficiency and corrosion rate of aluminium were investigated at varying temperatures and immersion time using thiourea complex with an organic ligand at concentrations of 0.20, 0.40, 0.60, 0.80 and 1.00 M. The results showed that an increase in the concentration of the complex thiourea led to an increase in the inhibition efficiency, which was attributed to the availability of the proton moiety of the thiourea lost as electron in acidic media. The inhibition efficiency decreased as the immersion time increased with temperature and the largest decrease observed at 333 K due to the distortion of molecular structure of the complex thiourea at high temperatures. The corrosion rate decreased with an increase in immersion time but increased with temperature, possibly due to inhibitor molecular rearrangement. The activation energy of the suppression process of high-concentration thiourea was found to be higher than that of low-concentration, indicating that the adsorption process was triggered by physical adsorption. The formation of a thin film on the metal surface was due to the presence of complex thiourea acted as a barrier to both energy and mass transport, leading to an increase in the activation energy. The adsorption of the thiourea derivatives complex on aluminum was primarily physisorption. The Langmuir, Flory-Huggins, Tempkin, and Dubinin-Radushkevich adsorption isotherm models were investigated with Langmuir found to be the most fitted model based on high R² values of the model.

Keywords: Ligand; Physisorption; Isotherm; Inhibition; Corrosion

1. Introduction
Corrosion is a significant challenge faced in both the industrial and domestic sectors, resulting in economic losses and posing threats to safety and health (Shirazi et al., 2023). Aluminium, a viable economic metal with vast applications in transportation, construction, and packaging, has shown to be highly susceptible to corrosion in acidic environments (Gummanar, 2023). Therefore, effective corrosion inhibitors are necessary to protect aluminium and extend its service life. These inhibitors which are substances that reduce corrosion rates by adsorbing on metal surfaces and forming a protective film are commonly used with organic inhibitors being effectively used on aluminium (Bentiss et al., 2005).

These organic inhibitors, composed of carbon, hydrogen, and oxygen, are less likely to form harmful byproducts, less likely to damage the metal surface, and more environmentally friendly than inorganic inhibitors. This is in line with growing trend of developing eco-friendly inhibitors which organic inhibitors positioned to do (Panchal et al., 2021). Thiourea Derivative, for example, has shown to be an interesting potential organic inhibitor moreso when complexed with various metals. These compounds have exhibited high corrosion inhibitory efficiency on copper, steel, and brass
in acidic media (Zhang et al., 2021). However, on aluminium, it is interesting to note there is a lack of comprehensive studies on the corrosion inhibitory properties of modified Thiourea Derivatives on aluminium in acidic environments.

Investigating the potential of thiourea derivatives as corrosion inhibitors for aluminium in acidic environments is necessary to develop highly efficient and eco-friendly inhibitors (Weder et al., 2016). Therefore, this study aims at evaluating the inhibitory properties of a thiourea derivative on aluminium in 0.1M HCl solution factoring its effect of concentration and temperature. The scope is to utilized the synthesized and characterized thiourea derivative for deducing its corrosion inhibitory properties of the thiourea derivative using weight loss techniques.

This study would significantly contribute to the development of effective and eco-friendly inhibitors that can protect aluminium in acidic environments. Also, providing some insight into the compound properties toward possible industrial applications.

2. Materials and method

2.1. Material Preparation

The current study involved the preparation of aluminum coupons of varying dimensions, obtained by cutting aluminum sheets. The coupons were subjected to abrasive grinding with abrasion paper ranging from 250 to 1000 grit. Subsequently, the coupons underwent thorough rinsing with distilled water and were cleaned again with high-purity solvents, including acetone (99% analytical grade) and ethanol (99% analytical grade). Following this, the coupons were allowed to dry for 12 hours in a desiccator. The prepared aluminum coupons were utilized in weight-loss experiments, representing an integral component of the research investigation.

2.2. Thiourea Derivative Preparation

The thiourea derivative, N-(2-hydroxylphenyl)-N′-(4-nitrobenzoyl) thiourea, had been synthesized and characterized by Fayomi et al. (2018). The synthesis adapted by dissolving 1.52 g of ammonium thiocyanate in 10 mL of acetone separately from 3.71 g of 4-nitrobenzoyl chloride was dissolved in 30 ml acetone. The two solutions were mixed gradually and heated under reflux for 2 hours before cooling. The reaction mixture was filtered and subsequently refluxed for an additional 2 hours and 2-aminophenol was added. Ice water was added to the precipitate the product, and recrystallized in a dichloromethane /ethanol solvent mixture. The product mixture was filtered, washed with water, and allowed to dry in a desiccator.

The synthesized product (thiourea derivative) was used for the preparation of media solutions at different molar concentration ranging from 0.02 to 0.10 M. The compound was initially dissolved in 5 mL of ethanol then 195 mL of 0.1 M HCl because of the non-polar nature of the compound.

2.3. Weight-loss Measurements

The previously cleaned and weighed aluminium coupons was immersed in corrosive media consisting of 0.1M of HCl (Analytical grade, 99.95%) and the thiourea derivative. The media solutions utilized were prepared at concentrations ranging from 0.20 to 1.00M and subjected to the aluminium samples for predetermined periods at both room temperature and temperatures of 313K, 323K, and 333K. Upon completion of the immersion periods, each sample was thoroughly washed with running water and ethanol, followed by drying within a dessicator, prior to the recording of their final masses. The protocol for this experiment was executed in accordance with NACE recommended Practice RP-0775 and ASTM G-1 and G-4 for weight-loss experimentation. The corrosion rate was determined from the recorded weight loss data, utilizing the following relationship.

2.3.1. Determination of inhibition efficiency of organic ligand complexed with thiourea

In exploring the corrosion inhibition effects of the thiourea derivative on aluminium in 0.1 M HCl media, the inhibition efficiency and corrosion rate were determined utilizing the gravimetric method, as previously reported by Ezeugo et al., (2017), with Equation (1) and (2), respectively. Additional references utilized for this work included Odejobi et al., (2019) and Hegde (2019).

\[ R_{corr} = \left( \frac{\Delta W}{A \cdot t} \right) \]

(1)

Here, \( \Delta W \) = weight loss, g/cm\(^2\)
A= area, cm$^2$
t= Immersion time in hours
D= density of the aluminium coupon (2.72/cm$^2$)
$R_{corr}$= corrosion Rate g/cm$^2$. Hr

The percentage efficiency of the inhibitors is taken as:

$$IE\% = \left(\frac{W_o - W}{W_o}\right) \times 100$$ (2)

Here $W_o$ = weight loss of the uninhibited aluminium in mg, $W$ = weight loss of the inhibited aluminium in mg

IE = inhibition efficiency in %

2.3.2. Determination of Activation Energy ($E_a$)

In accordance with Equation (3), a plot of the logarithm of corrosion rate, $R_{corr}$, against the reciprocal of absolute temperature, $1/T$, was generated to determine the activation energy, $E_a$. The relationship between corrosion rate ($R_{corr}$) and temperature ($T$) is described by the Arrhenius equation, as previously reported by Louise and colleagues (2017).

$$\log R_{corr} = \left(\frac{-E_a}{2.303RT}\right) + \log \gamma$$ (3)

here, $E_a$ = activation energy,
$R$ = gas constant
$T$ = temperature in kelvin and
$\gamma$ = exponential factor.

2.3.3. Determination of Enthalpy and Entropy change

Equation 4, an alternative form of the Arrhenius equation in the transition state, was utilized to determine the enthalpy change and entropy change. This approach has been previously reported by Guo and colleagues (2017).

$$R_{corr} = \frac{RT}{Nh} \exp(\Delta S/R) \exp\left(-\frac{\Delta H}{RT}\right)$$ (4)

Equation (4) is linearized, thus:

$$\log \left(\frac{R_{corr}}{T}\right) = \log \left(\frac{R}{Nh}\right) + \log e^{\frac{\Delta S}{R}} + \log e^{\frac{-\Delta H}{RT}}$$ (5)

Since $\log(exp(x)) = x \div \ln 10$

Therefore, Equation (4b) becomes

$$\log \left(\frac{R_{corr}}{T}\right) = \log \left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{Rln10}\right) + \log \left(\frac{-\Delta H}{2.303R}\right)$$ (6)

$$\log \left(\frac{R_{corr}}{T}\right) = -\left(\frac{\Delta H}{2.303R}\right) \left(\frac{1}{T}\right) + \log \left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{Rln10}\right)$$ (7)

Here $h$ = plank's constant,
$N$ = Avogadro's number,
$\Delta S$ = entropy change
$\Delta H$ = enthalpy change

The enthalpy change, $\Delta H$, was determined by analyzing the slope $\left(\frac{-\Delta H}{2.303R}\right)$ of the graph of $\log \left(\frac{R_{corr}}{T}\right)$ against $\left(\frac{1}{T}\right)$. Likewise, the entropy change, $\Delta S$, was calculated by analyzing the intercept $\log \left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{Rln10}\right)$ of the graph.
2.4. Adsorption Isotherm and Adsorption Constant

Adsorption studies were performed to elucidate the mechanism by which the inhibitor adsorbs onto the metal surface (Belkhaouda, et al., 2013). The adsorption behavior of thiourea complexed with organic ligand on aluminium in 0.1 M HCl media was analyzed using various adsorption isotherm models, including Langmuir, Temkin, Freundlich, Frumkin, El Awwady, and Flory-Huggins adsorption isotherms. The most appropriate model that describes the adsorption process was determined by fitting the corrosion rate, \( R_{corr} \), and the degree of surface coverage of the inhibitor, \( \Theta \) (which is the reciprocal of inhibition efficiency), into the linear forms of the adsorption isotherm models.

The Langmuir adsorption isotherm model (Dagadag et al., 2019; Nwabanne et al., 2012)

\[
R_{corr} + \Theta = (1 + K_{ads}) + R_{corr}
\] (8)

Frumkim adsorption isotherm and model (Nwabanne et al., 2012).

\[
\log \left[ R_{corr} \left( \Theta + \frac{1}{\Theta} \right) \right] = 2\alpha\Theta + 2.303 \log K_{ads}
\] (9)

El-Awdy's thermodynamic/Kinetic adsorption isotherm model (Nwabanne et al., 2012; Chauhan, et al., 2006):

\[
\log \left[ R_{corr} \left( \Theta + \frac{1}{\Theta} \right) \right] = y \log R_{corr} + \log K
\] (10)

\( K_{ads} = K \left( \frac{1}{y} \right) \)


\[ \Theta = \ln R_{corr} + K_{ads} \] (11)


\[ \log \Theta = \log K_{ads} + n \log R_{corr} \] (12)


\[ \log \left( \Theta / R_{corr} \right) = b \log \left( 1 - \Theta \right) + \log K_{ads} \] (13)

2.5. Thermodynamics Parameters

In order to investigate the feasibility and nature of the adsorption, Equation (12) proposed by Fathi et al., 2008, was utilized to express the Gibbs free energy change of adsorption.

\[ \Delta G_{ads} = - RT \ln (55.5 K_{ads}) \]

The adsorption equilibrium constant, \( K_{ads} \), which is derived from the isotherm, is multiplied by 55.5, which represents the molar concentration of water in the solution.

3. Result and Discussion

Figure 1 show the inhibition efficiency and corrosion rate at varying temperatures and immersion times with thiourea complexed with an organic ligand at concentrations of 0.20, 0.40, 0.60, 0.80, and 1.00 M. The inhibition efficiency increased with an increase in the concentration of the complexed thiourea, which can be attributed to the availability of the proton moiety of the organic ligand complexed to thiourea for electron loss in acidic media. This availability reduces the rate of ion adsorption to the metal surface. The lowest inhibition efficiency was recorded at 0.20 M and the highest at 1.00 M, while as the immersion time increased, the inhibition efficiency decreased. However, the inhibitory effect decreased with temperature for each immersion time, with the largest decrease at 333 K. This decrease may be due to the distortion of the molecular structure of the complexed thiourea at high temperatures. Moreover, an increase in temperature increases the solubility of the protective layer of the metal, resulting in increased metal sensitivity to corrosion, as reported by Amal et al. (2021). The corrosion rate was observed to decrease with an increase in immersion time and increase with temperature. This observation is attributed to the downward progression of reaction rates with time and upward progression with temperature due to an increase in the average kinetic energy of the reacting
molecules. The increase in corrosion rate may also be due to an increase in inhibitor molecular rearrangement. The inhibitory effect decreased with increasing temperature, as is common with most organic inhibitors, owing to changes such as inhibitor molecular rearrangement on the metal surface when the reaction is inhibited at high temperatures. Temperature fluctuations were found to affect metal dissolution, inhibitor adsorption/desorption, and inhibitor efficiency, as reported by Tang et al. (2019).

3.1. Activation energy (Ea)

The experimental data displayed a perfect fit in the plots of log Cr against 1/T for extract concentrations of 0.20, 0.40, and 0.80 M, indicating the consistency of the results. Consequently, the gradient derived from the curve is suitable for estimating the activation energy of the process at different temperatures for the same immersion time. Table 1 presents the activation energy (Ea) evaluated at the same immersion time for various concentrations of complexed Thiourea at temperatures of 313, 323, and 333 K. As shown in the table, the activation energy of the suppression process of high-concentration complexed Thiourea is higher than that of low-concentration, suggesting that the adsorption process is triggered by physical adsorption. The increased energy barrier associated with the higher Ea value in the presence of the inhibitor confirms the formation of a complex compound between the inhibitor and aluminum.

<table>
<thead>
<tr>
<th>Conc(M)</th>
<th>Ea (KJ/mol)</th>
<th>ΔH (KJ/mol)</th>
<th>ΔS (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>729.1</td>
<td>72.4</td>
<td>-131.3</td>
</tr>
<tr>
<td>0.04</td>
<td>-175.2</td>
<td>-42.3</td>
<td>135.6</td>
</tr>
<tr>
<td>0.08</td>
<td>-184.1</td>
<td>-426.4</td>
<td>138.9</td>
</tr>
</tbody>
</table>

The obtained result suggests that the presence of complexed thiourea can lead to the suppression of corrosion by increasing the energy barrier of the metal dissolution process. This is due to the formation of a thin film on the metal surface, which acts as a barrier to both energy and mass transport, and subsequently increases the activation energy. Therefore, the findings of the study indicate that the adsorption of the organic ligand complexed with thiourea on aluminum is primarily caused by physical adsorption. The analysis of Table 9 shows that the activation energy decreases with increasing inhibitor concentration. However, it is noteworthy that the activation energy is still higher than that of the thiourea complex at a concentration of 0.20 M. These findings are consistent with the previous research conducted in this area.
3.2. Enthalpy and Entropy Change
The values of enthalpy change $\Delta H$ and entropy change $\Delta S$ obtained at different temperatures and immersion times are presented in Table 9. The resulting $\Delta H$ value was positive and observed to decrease with increasing inhibitor concentration. Conversely, the entropy value at the 3-hour immersion time was negative, indicating a reduction in disorder in the transition from the reactants to the activated complex. This result is consistent with the findings of Sudhish et al. (2011).

The activation energy ($E_a$) value over the enthalpy change ($\Delta H$) were considered. This suggest that the corrosion process was accompanied by a gas reaction. The average value ($E_a - \Delta H$) of the difference between the activation energy and the enthalpy change was found to be $26.1 \pm 2.61$ kJ/mol at the immersion time of 3 hours, which is equivalent to the product of the gas constant ($R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$) and the average temperature of the experiment ($T = 314 \text{ K}$). This was calculated using the formula $E_a - \Delta H = RT$. The result obtained is consistent with the study conducted by Menzri et al. (2017), who reported that the corrosion process is a monomolecular reaction involving the generation of hydrogen gas.

3.3. Adsorption Isotherms

The present study investigated various adsorption isotherm models, as depicted in the figure. The determination of the most appropriate model was based on the $R^2$ values of each isotherm model, as presented in Table 8. The results revealed that the Langmuir, Flory-Huggins, Tempkin, and El-Awađy's isotherms could effectively describe the data obtained. However, the Tempkin adsorption isotherm displayed the best fit with an $R^2$ value of approximately 0.99.
Thus, it can be concluded that the adsorption of the thiourea complex on aluminum and its metal alloys in hydrochloric acid can be best explained by the Tempkin adsorption isotherm. Consequently, the Tempkin adsorption isotherm can be employed to determine the adsorption equilibrium constant $K_{ads}$.

![Figure 3 Thermodynamic plot of ln K against 1/T x 10^-3 for the adsorption of thiourea complex](image)

3.4. Adsorption Equilibrium Constant

The present study investigates the adsorption equilibrium constants of inhibitors on the metal surface at various temperatures, as shown in Table 10. The obtained adsorption equilibrium constant $K_{ads}$ values are positive, indicating the possibility of successful adsorption of inhibitors on the metal surface. The $K_{ads}$ values initially increase with temperature until 323 K. However, as reported by Hegazy et al. (2011), the $K_{ads}$ values decrease at 333 K, indicating that the adsorbed inhibitors tend to desorb from the aluminum surface at high temperatures. This observation further validates the activation energy values obtained from previous calculations.

3.5. Gibb's Free Energy Change of Adsorption

The presented table depicts the alterations in the free energy of adsorption, $\Delta G_{ads}$, assessed at various temperatures. The table indicates that the values of $\Delta G_{ads}$ are negative and do not exceed 20 kJ/mol. This outcome implies that the adsorption process of thiourea complex onto the aluminum surface is spontaneous and feasible and transpires according to the physical adsorption mechanism. A decrease in $\Delta G_{ads}$ at 333 K implies a reduction in the spontaneity and stability of the adsorption process at higher temperatures.

4. Conclusion

The evaluation the effectiveness of $N$-(benzoylcarbamothioyl) thiourea derivative, synthesized through the reaction of 4-nitro-benzoyl isothiocyanate with amino acids (glycine), in inhibiting the corrosion of aluminium under various concentrations, immersion time, and temperatures. The corrosion inhibition performance was assessed via gravimetry or weight loss analysis, revealing that a mixture of $N$-(benzoylcarbamothioyl) derivative exhibits notable inhibitory properties towards the corrosion of aluminium in 0.1M HCl with a maximum corrosion inhibition efficiency of approximately 95.55 % observed at an inhibitor concentration of 1.00 M. Furthermore, the adsorption behaviour of inhibitor on the aluminum surface was found to comply with the Tempkin adsorption isotherm, suggesting that the adsorption process is of physical nature and endothermic process.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.
References


