Corrosion inhibition effect of 1-thia-3-azaindene on type 304 austenitic stainless steel in 3M H₂SO₄ solution

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Abstract. Corrosion inhibition of 1-thia-3-azaindene (T3A) on type 304 austenitic stainless steel was studied in 3 M H₂SO₄ solution at specific concentrations by potentiodynamic polarization. Results showed T3A performed effectively with optimal inhibition efficiency of 92.58% at 1.5% volumetric concentration with the corresponding corrosion rate of the steel at 0.53 mm/y compared to 6.72 mm/y in the acid solution without T3A compound. Inhibition performance increased with inhibitor concentration. T3A exhibited anodic type chemisorption inhibition according Langmuir, Temkin, Frumkin and Freundlich adsorption isotherms with correlation coefficient generally above 0.9. Polarization plots showed significant passivation behaviour after metastable pitting activity before breakdown at pitting potential signifying extensive surface coverage of the steel. The cathodic portion of the polarization plot showed H₂ evolution and O₂ reaction mechanisms are under activation control.

1. Introduction
Stainless steels generally have higher resistance to corrosion than carbon steels due to the formation of an inert protective oxide on steel surfaces [1, 2]. However, there are industrial condition harmful to stainless steels and significantly decrease their lifespan during operation. The huge financial and economic cost resulting from corrosion of stainless steels is a major problem and is the focus of research into more resistant steels and cost effective corrosion control techniques [3-5]. The huge cost is due to accelerated breakdown of the steel locally leading to unforeseen industrial accidents, high cost of maintenance and constant repairs [6, 7]. Industries such as oil and gas, petrochemical, fertilizer production, chemical processing, marine and shipping, heat exchangers and energy generation experience huge corrosion problems due to the presence of highly reactive corrosive species such as S₂O₃(2-), Cl⁻, SO₄²⁻, NO₃⁻ etc. [8, 9]. Type 304 austenitic stainless steel have extensive application due to its excellent mechanical properties, weldability, formability and corrosion resistance [10, 11] especially for power plant components, chemical containers and heat exchangers. Heterocyclic compounds and compounds of organic origin have been proven to be excellent corrosion inhibitors. [12-22]. However, more research is needed to develop high performance inhibition at very low concentration with chemisorption type inhibition mechanism in industrial environments. In contribution to the research on application of corrosion inhibitor for stainless steels this article focusses on the corrosion inhibition performance of 1-thia-3-azaindene compound on austenitic steel in 3M H₂SO₄.

2. Experimental methods
Type 304 austenitic stainless steel (AISI 304) rod procured from Lagos, Nigeria was analysed at the Materials Characterization Laboratory, Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria to determine its composition shown in Table 1. AISI 304 was machined into 7 samples which underwent metallographic preparation before being encased in Versocit acrylic paste. 1-thia-3-azaindene (T3A), a translucent liquid compound was obtained from BOC Chemicals, USA. It has a
molecular weight of 135.19 g/cm$^3$. The structural configuration of the compound is shown in Fig. 1. T3A was added to 3 M H$_2$SO$_4$ (98% analar grade) in volumetric concentrations of 0.25%, 0.5%, 0.75%, 1%, 1.25% and 1.5% T3A concentration per 400 mL of the acid solution.

Table 1. Elemental content (wt. %) of AISI 304

| Element | C | Cr | Mn | Si | P | S | Ni | N | Fe |
|---------|---|----|----|----|---|---|----|---|----|
| Composition | 0.07% | 18.5% | 2% | 1% | 0.045% | 0.0015% | 9% | 0.01% | Balance |

Potentiodynamic polarization was test was utilized with the aid of three electrode system (Pt counter electrode, AISI 304 specimen electrode and Ag/AgCl reference electrode) placed within a visible container with the T3A/H$_2$SO$_4$ solution and connected to Digi-Ivy potentiostat/computer system for real-time monitoring from -1.5V to +1.5 mV at scan rate of 0.0015V/s. Corrosion current ($I_c$) A, corrosion current density ($J_c$) A/cm$^2$, corrosion potential ($P_c$) V, anodic and cathodic Tafel slope ($B_a$ and $B_c$) V/dec and polarization resistance ($R_p$) Ω were computed from the Tafel plots and the data output. Corrosion rate ($R_c$) was calculated as follows

$$R_c = \frac{0.00327 \times D}{\sqrt{\rho}}$$  

$D$ (g/cm$^3$) indicates density and $E_{WT}$ (g) indicates AISI 304 equivalent weight in grams. Inhibition efficiency ($I_e$) was computer from the equation below;

$$I_e = 1 - \left(\frac{C_2}{C_1}\right) \times 100$$

$C_1$ and $C_2$ represents corrosion rate with and without T3A addition.

3. Results and discussion

3.1 Potentiodynamic polarization

Potentiodynamic polarization plots of AISI 304 in 3M H$_2$SO$_4$ solution at predetermined concentrations of T3A are shown in Fig. 2. Table 2 shows the data for the electrochemical parameters obtained from the polarization test. Table 2 shows the significant difference between the corrosion rate of AISI 304 at 0% T3A and the corrosion rate values at 0.25% to 1.5% T3A. At 0% T3A the corrosion rate value of AISI 304 (6.72 mm/y) is due to oxidation of AISI 304 surface resulting from the breakdown of the inert protective oxide on the steel surface. SO$_4^{2-}$ anions in the acid solution diffuse through the metal/solution interface displacing the adsorbed O$_2$ atoms responsible for the formation of the protective oxide. This redox electrochemical process exposes the substrate Fe metal to localized corrosion deterioration as the surface deterioration first starts at regions or sites where impurities, inclusions etc. are present. The impurities cause discontinuities in the protective oxide leading to pit initiation and eventual growth of the steel surface area exposed to corrosion. Addition of T3A compound to the acid solution significantly reduced the corrosion rate of AISI 304 with respect to T3A concentration. At 0.25% T3A concentration, the corrosion rate of AISI 304 is 3.59 mm/y corresponding to inhibition efficiency of 49.46% and polarization resistance of 83.3Ω. This value is below the value for effective corrosion inhibition. However, beyond 0.25% T3A concentration, significant decrease in corrosion rate coupled with significant increase in inhibition efficiency was observed. The corrosion rate and inhibition efficiency of AISI 304 and T3A at 0.5% T3A were 2.51 mm/y and 64.76%. At 0.75% T3A, the values are 1.80 mm/y and 74.73% while at optimal T3A concentration of 1.5% the values are 0.53 mm/y and 92.58%. Observation of the polarization resistance values show significant increase in value from 29.26Ω at 0% T3A to 433.0Ω at 1.5% T3A. Variation in corrosion potential from between values at 0.25% to 1.5% T3A and the value at 0% T3A shows significant anodic shift from 0.25% T3A to 1% T3A due to suppression of the oxidation reactions on the steel surface. This assertion is further confirmed from the significant variation of the anodic portion of the polarization plots. Whereas observation of the cathodic portion of the polarization plots shows near similarities signifying that the cathodic reaction mechanisms are under activation control. The maximum variation in corrosion potential is between T3A concentration at 0% and 1% concentration i.e. 135mV in the anodic direction which shows the inhibition mechanism of T3A aligns with anodic type inhibition. This is proven from the passivated region on the anodic portion of the polarization plot from 0.25% T3A concentration. Observation of the plots in Fig. 2 shows the onset and propagation of metastable pitting before passivation, passivated region and pitting corrosion. At 0.25% T3A metastable pitting occurred before passivation. However, immediately after passivation breakdown occurred due to pitting corrosion of the steel surface.
Starting from 0.25% T3A to 1% T3A, it is observed that there is metastable pitting before passivation of the steel, increase in T3A concentration slightly increased the passivated region before breakdown due to pitting. Peak passivation behaviour was observed at 1% T3A. Beyond 1% T3A, significant decrease in the passivated region occurred at 1.25% T3A while at 1.50% T3A the passivated region has almost completely disappeared despite decrease in corrosion rate and increase in inhibition efficiency due to lateral interaction mechanism among inhibitor molecules which influenced their selective precipitation performance.

**Figure 2** Potentiodynamic polarization plot of AISI 304 corrosion in 3 M H2SO4 solution at specific T3A concentration

**Table 2.** Data on weight-loss of AISI 304 from 1M H2SO4/TD (0% - 0.015%) solution

| Sample | T3A Conc. (%) | AISI 304 C_R (mm/y) | T3A IE (%) | C_I (A) | C_P (A/cm²) | R_p (Ω) | B_a (V/dec) | B_a (V/dec) |
|--------|---------------|---------------------|------------|---------|--------------|--------|-------------|-------------|
| A      | 0             | 6.72                | 0          | 5.15E-04 | 6.54E-04     | 29.76  | 7.803       | 0.035       |
| B      | 0.25          | 3.59                | 49.46      | 2.76E-04 | 3.50E-04     | 83.30  | 5.647       | 0.965       |
| C      | 0.5           | 2.51                | 64.76      | 1.92E-04 | 2.44E-04     | 102.96 | 4.415       | 0.123       |
| D      | 0.75          | 1.80                | 74.73      | 1.38E-04 | 1.75E-04     | 185.80 | 5.178       | 5.193       |
| E      | 1             | 1.33                | 81.23      | 1.02E-04 | 1.30E-04     | 262.70 | 4.572       | 0.754       |
| G      | 1.25          | 0.85                | 88.03      | 6.53E-05 | 8.29E-05     | 342.30 | 8.780       | 5.150       |
| H      | 1.5           | 0.53                | 92.58      | 4.05E-05 | 5.14E-05     | 433.00 | 9.361       | 7.530       |

3.2 Adsorption Isotherm

Adsorption and corrosion inhibition effect of T3A on AISI 304 is due to the ability of protonated T3A molecules in H2SO4 solution to displace H2O molecules on the steel surface, hinder the electrolytic transport of SO₄²⁻ unto the steel surface and suppress the redox reaction mechanisms responsible for corrosion. Further insight into the inhibition behavior is gotten from mathematical models known as adsorption isotherms which depict show the quantitative variation of protonated T3A ionic species adsorbed unto AISI 304 under equilibrium conditions [23]. The strength of T3A adsorption onto AISI 304 is determined by the strength of the electrostatic attraction between T3A and the steel surface. The presence of polar functional groups with S, and N atoms in the inhibitor molecule of the aromatic heterocyclic compound and pi electrons reacts with the valence electrons on the steel surface resulting in strong covalent bond [24, 25]. AISI 304 in the acid solution causes the accumulation of SO₄²⁻ anions at the metal/solution interface resulting in excess -ve charges on the steel surface. The negative charge on the steel strongly attracts the protonated inhibitor molecule leading to strong impenetrable chemical complex/precipitate on the steel
stifling further electrochemical reaction. Results from potentiodynamic polarization were used to determine the appropriate adsorption isotherm for T3A adsorption. Langmuir, Frumkin, Freundlich and Temkin gave appreciable correlation coefficient values. The values are shown in Table 3.

| Adsorption Isotherms | H₂SO₄ Solution |
|----------------------|----------------|
| Langmuir            | 0.9964         |
| Frumkin              | 0.7424         |
| Freundlich           | 0.9611         |
| Temkin               | 0.9979         |

The Langmuir, Frumkin, Freundlich and Temkin isotherms are shown from Figs. 3(a) to 4(b). Langmuir isotherm states a definite quantity of locations on metallic surfaces exist for adsorption of single layer molecules exhibiting fixed energy value in variable equilibrium according to the equation below;

\[ \theta = \frac{K_{ads}C_{T3A}}{1+K_{ads}C_{T3A}} \]  

(3)

\( K_{ads} \) is the equilibrium constant of adsorption during the inhibition process. \( C_{T3A} \) is the molar concentration of T3A compound. According to Temkin isotherm the heat of adsorption progressively decreases as molecular increases with equivalent binding energy distribution [26], according to the equation below;

\[ q_e = B \ln (A + C_e) \]  

(4)

Where \( B = RT/b \)  

(5)

\( A \) indicates Temkin isotherm constant (L/g), \( b \) indicates Temkin constant related to heat of adsorption, \( T \) indicates temperature (K), \( R \) represents gas constant (8.314, J/mol K) and \( C_e \) represents concentration of adsorbate. \( B \) indicates the Temkin constant related to heat of sorption (J/mol). Frumkin isotherm states that molecular coverage on non-homogeneous adsorbent surfaces is similar under high molecular concentrations with respect to the potential of the adsorbent surface. The effect of lateral attraction/repulsion between inhibitor molecules is significant and quantitative according to the equation below;

\[ \log [C_{T3A} * (\frac{\theta}{1 - \theta})] = 2.303 \log K_{ads} + 2a\theta \]  

(6)

\( \alpha \) is the lateral interaction parameter. The Freundlich isotherm states that adsorbed molecular interaction exist on adsorbent metal surfaces and the lateral attraction/repulsion between them occurs [27]. The Freundlich equation is stated as follows;

\[ \theta = KC^n \]  

(7)

\[ \log \theta = n \log C + \log K_{ads} \]  

(8)

\( n \) represents the constant for the characteristics of adsorbed T3A molecule
Figure 3 Adsorption isotherm plot (a) Langmuir isotherm and (b) Temkin isotherm

Figure 4 Adsorption isotherm plots (a) Frumkin isotherm and (b) Freundlich isotherm

Data for Gibbs free energy (ΔG) representing the adsorption strength of T3A onto AISI 304 surface in H₂SO₄ are presented in Table 4. The results were calculated from the formula below. Equilibrium constant of T3A adsorption (K_{ads}) was gotten from the Langmuir due to its high correlation coefficient value.

\[
\Delta G_{ad} = -2.303RT \log [55.5K_{ad}]
\]  

55.5 indicates the molar concentration of H₂O in the solution, R is the universal gas constant, T is the absolute temperature. The ΔG values depict chemisorption adsorption of T3A compound unto AISI 304 signifying strong electrostatic attraction and covalent bonding [28, 29]. The values also show T3A effectively displaced H₂O molecules from the aqueous solution and suppression of SO₄²⁻ displacement reactions. The potentiodynamic plots give evidence for competitive adsorption between the inhibitor molecules and corrosive species. The ΔG values ranges from (lowest to highest) -36.75 KJmol⁻¹ to -37.91 KJmol⁻¹ signifying chemisorption. However, the values are not proportional to T3A concentration signifying lateral interaction effect occurs irrespective of T3A concentration.
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