Electrochemical performance of 2-mercaptobenzothiazole on the corrosion inhibition of selected metallic alloys in dilute acid media

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Abstract: The inhibition performance of 2-mercaptobenzothiazole on the corrosion of 316 austenitic stainless steel in 3M HCl, mild steel in 1M HCl and 1060 aluminium alloy in 2M H₂SO₄ solution alloy was studied by coupon measurement. Results showed the compound performed more effectively on the 316 steel with average corrosion inhibition performance result of 90% followed by the aluminium alloy with average inhibition performance value of 70%. 2-mercaptobenzothiazole performed poorly on mild steel with average inhibition performance results of 55% at low concentration and results below 0% and high inhibitor concentrations. Statistical data through showed that inhibitor concentration only influenced the inhibition performance of 2-mercaptobenzothiazole. Inhibitor concentration and exposure time were statistically relevant to the inhibition performance of 2-mercaptobenzothiazole on mild steel at varying degrees while both inhibitor concentration were statistically irrelevant to the inhibition performance of 2-mercaptobenzothiazole on 1060 aluminium alloy. Adsorption isotherm studies showed SD adsorption on the metallic alloys aligned with Langmuir, Frumkin and Freundlich adsorption with general correlation coefficient above 0.9991.

Keywords: corrosion; steel; aluminium; 2-mercaptobenzothiazole; HCl; H₂SO₄.

1. INTRODUCTION

Stainless steels, carbon steels and aluminum alloys are used in the design, fabrication and building of machinery, parts, components and structures with respect to design and performance requirements, specific nature of application, industrial operating conditions and end use environmental factors due to their possession of specific mechanical, physical, metallurgical and aesthetic properties. Stainless steels are metallic alloys with Cr content higher than 10.5%. They have a wide variety of applications in hot-water tanks, automotive, petrochemical, marine, mining, energy generation and chemical processing plants [1]. They are generally known for their corrosion resistance in industrial environments where carbon steels exhibit weak corrosion resistance. Their corrosion resistance is due to the formation of an inert, impenetrable protective oxide on the steel surface [2, 3]. Stainless steels are however subject to localized corrosion deterioration in the presence of chlorides, sulphates, thiosulphates etc. causing the protective film to breakdown or unable to reformed instantaneously in the presence of the corrosive anions. Carbon steels have seen extensive use for structural components, parts and systems due to their relatively low price, availability, recyclability and easy formability [4]. The weak corrosion resistance of carbon steels in aqueous environments is a huge setback to their operational lifespan. Aqueous environments are encountered in industrial operations such as pickling...
and descaling in mining operations, and petrochemical drilling operations crude distillation refinery operations, desalination plants etc. [5]. Aluminium alloy is extensively used for general industrial components, in civil engineering, electrical and communication cables, heat exchangers and aerospace [6]. The extensive use of aluminium is due to its strength-density ratio, relative light weight, toughness and corrosion resistance. The complicated corrosion reaction mechanism and deterioration of aluminium alloy is the subject continuous research due to its importance in the current technological development worldwide [7]. Aluminium is an amphoteric metal, its corrosion resistance results from the initiation and growth of a protective oxide film on its surface [8]. The cost of corrosion is enormous and unsustainable. The direct cost of corrosion worldwide is estimated to be about €1.4 trillion. This value does excludes the cost of environmental damage, wastage of resources, loss of production, or personal injury resulting from corrosion [9]. Corrosion of stainless steels causes immense economic damage. Corrosion is responsible for about 1/3 of the total annual metal scrap produced globally. Corrosion causes perforation of pipelines and containers resulting in leakage toxic chemicals to the environment. Internal pipeline damage due to corrosion is for about 15% of all pipeline deterioration in the United States [10-12]. Corrosion can be significantly minimized with the use of chemical compounds known as corrosion inhibitors which altered the chemical composition of the corrosive environment making it less corrosive and simultaneously hindering the electrochemical interaction between the metallic alloy and its environment. The manuscript focuses on the inhibition performance of 2-mercaptobenzothiazole on 316 austenitic stainless steel, low carbon steel and 1060 aluminum alloy in dilute HCl and H2SO4 solution.

2. MATERIAL AND METHODS

316 austenitic stainless steel (AS316), mild steel (MS) and 1060 aluminium (1060A) rods were machined and prepared into 7 separate specimens for coupon measurement. Sulfadene (SD), obtained from BOC Chemicals, USA was formulated in volumetric concentrations from 0% (no SD compound), 0.19%, 0.25%, 0.31%, 0.38%, 0.44% and 0.50% per 200ml of 3M of HCl for AS316. SD was formulated in volumetric concentrations of 0%, 0.75%, 1%, 1.25%, 1.5%, 1.75% and 2% per 200ml of 1M HCl for MS while for AL1060; the SD was formulated in volumetric concentrations of 0%, 0.19%, 0.25%, 0.31%, 0.38%, 0.44% and 0.50% per 200ml of 2M H2SO4. Weighed AS316, MS and 1060A test specimens were placed within 200ml of the electrolyte solution for a total exposure period of 384 h. AS316, MS and 1060A were weighed at 48 h interval to obtain the weight loss result. The weight loss is the difference between the initial weight of the metal specimen (retained for 384 h) and the final weight obtained at 48 h interval. Inhibition efficiency (\( \eta \)) was determined from the equation below;

Corrosion rate, \( C_R \) (mm/y) was calculated from the equation below;

\[
C_R = \frac{87.6 \omega}{DAt}
\]  

(1)

\( \omega \) represents weight loss (g), \( D \) represents density (g/cm\(^3\)), \( A \) represents total surface area of MS specimen (cm\(^2\)), 87.6 is a corrosion rate constant and \( t \) represents time (h). Inhibition efficiency (\( \eta \)) was calculated as follows;

\[
\eta = \left(\frac{W_1-W_2}{W_1}\right) * 100
\]  

(2)

\( W_1 \) and \( W_2 \) are the weight-loss of the control and inhibited metal specimen within the electrolyte per exposure time.
3. RESULTS AND DISCUSSION

3.1 Coupon measurement

Figures 1(a) and (b) shows the plot of AS316 corrosion rate and SD inhibition of AS316 corrosion versus exposure time in 3M HCl solution. Figures 2(a) and (b) shows the plot of MS corrosion rate and SD inhibition of MS corrosion versus exposure time in 1M HCl solution while Figures 3(a) and (b) shows the plot of 1060A corrosion rate and SD inhibition of 1060A corrosion versus exposure time in 2M H2SO4 solution. Observation of the plots in Figure 1(a) shows the significant difference between the plots of AS316 at 0% SD and plots at 0.38% - 1% SD. AS316 plot at 0% SD is due to the oxidation AS316 surface as a result of the electrochemical action of Cl- ions which results in the release of Fe ions into the electrolyte and evolution of H2 gas resulting from reduction reaction processes. The corrosion rate plot decreased sharply from 2.36 x 10^-3 mm/y at 48 h to 5.87 x 10^-4 mm/y at 144 h, beyond this point the decrease is gradual due to weakening of the electrolyte solution with the corrosion products. The corrosion rate for AS316 at 0.38% - 1% SD varies between 5 x 10^-4 mm/y (0.38% SD) and 2.3 x 10^-4 mm/y (1% SD) at 48 h of exposure. The corrosion rates at all SD concentrations decreased to average values 6.5 x 10^-6 mm/y at 144 h and 2.1 x 10^-6 mm/y at 384 h. The corrosion rate of AS316 at 0% SD at 384 h of exposure is 6.92 x 10^-5 mm/y. Observation of the corresponding SD inhibition efficiency plots shows SD compound effectively inhibited AS316 corrosion with respect to its concentration. The highest inhibition efficiency result was obtained at 1% SD concentration while the lowest was obtained at 0.38% SD. However, the average inhibition efficiency value is generally above 90%. At 48 h, the inhibition efficiency varies between 87.6% (1% SD) and 75.9% (0.38%) before peaking at values of 96.31% and 93.18% at 384 h of exposure.

SD compound performed poorly on MS as shown in Figure 2(a) and (b). Observation of the corrosion rate results shows SD is only effective at low concentrations (0.75% SD, 1% SD and 1.25% SD). Beyond 1.25% SD concentration, the corrosion rates were significantly high, even higher than the corrosion rate at 0% SD. The general configuration of the corrosion rate plots simply shows SD performance is irregular and unstable on MS in 1 M HCl solution. The corresponding inhibition efficiency plots present more detail on the inhibition performance of SD on MS in the electrolyte. The plots show that SD at 0.75% to 1.25% concentration initiated very poorly at -20.32%, 4.63% and -8.73% (48 h) before progressing to average peak values of 57.75% at 384 h of exposure. The final values show SD is generally ineffective in inhibiting MS corrosion in HCl compared to its performance on AS316, where the inhibition efficiency values are generally above 90%.

SD effectively inhibited 1060A corrosion in 2M H2SO4 solution as shown in the plots in Figure 3(a) and (b). The corrosion rate plot at 0% SD starkly contrasts the plots at 0.19% and 0.5% SD concentration. The plot at 0% SD initiated (48 h) at 2.184 mm/y and decreased to 1.229 mm/y at 144 h before sharply increasing to 3.756 mm/y at 384 h. This is due breakdown of the protective oxide on 1060A surface. The initial decrease in corrosion rate of 1060A is due to growth of the protective oxide. However, the protective oxide is not resilient in the presence of continuous attack from SO4^2- anions in the acid solution. As a result the rate of growth and formation of the oxide is much slower than the rate of breakdown of the oxide film leading to accelerated corrosion which later occurred. The corrosion rate plots at various concentrations of SD initiated (48 h) at various values before peaking (384 h) at 0.735 mm/y (0.38% SD concentration) and 1.080 mm/y (0.25% SD concentration). The corresponding inhibition efficiency values shows SD performance varies between 70.6% at 0.25% SD concentration and 79.77% at 0.31% SD concentration. The inhibition efficiency plots show progressive increase in inhibition value with respect to exposure time at all SD concentration signifying effective inhibition performance.
Figure 1. Plots of (a) AS316 corrosion rate versus exposure time and (b) SD inhibition efficiency versus exposure time from 3M HCl solution.

Figure 2. Plots of (a) MS corrosion rate versus exposure time and (b) SD inhibition efficiency versus exposure time from 1M HCl solution.
3.2 Analysis of variance (ANOVA)
Anova analysis at 95% confidence level (significance level of $\alpha = 0.05$) was employed to determine the statistical relevance of SD% concentration and exposure time on the inhibition performance of SD compound on AS316, MS and 1060A with respect to the equations (3 - 5) below.

The Sum of squares among SD concentration

$$SS_c = \frac{\sum r^2}{nr} - \frac{\sum r^2}{N}$$  \hspace{1cm} (3)

Sum of Squares among exposure time

$$SS_r = \frac{\sum r^2}{nc} - \frac{\sum r^2}{N}$$  \hspace{1cm} (4)

Total Sum of Squares

$$SS_{Total} = \sum x^2 - \frac{\sum r^2}{N}$$  \hspace{1cm} (5)

Anova results depicting the influence of SD concentration and exposure time on the inhibition performance of SD on the metallic alloys are shown from Tables 1 to 3. Table 1 showed that SD concentration is the only important statistical variable responsible for SD inhibition performance on AS316 with significance factor value ($F$-value) of 10.52 [13]. The value is significantly higher than the control significance factor (significance $F$) value of 2.42, corresponding to a percentage significance of 111.04%. The result shows exposure time with significance factor value of -5.87 and percentage significance of -74.37 is irrelevant on the inhibition performance of SD compound on AS316. Variation in SD concentration has strong influence the electrochemical corrosion behavior and inhibitor protection of SD on AS316. Table 2 shows that SD concentration and exposure time are statistically relevant at varying degrees on the inhibition performance of SD compound on MS with significance factor values higher than the control significance factor. SD concentration has significance factor value of 7.76 and percentage significance of 45.22 while for the corresponding exposure time the significance factor value is 2.84 and percentage significance is 19.84%. The results show that the statistical relevance of both independent variables is below 50% though SD concentration is significantly higher is relevance than exposure time. Observation of Table 3 shows...
SD concentration and exposure time are statistically irrelevant on the inhibition performance of SD compound on 1060A in 2M H$_2$SO$_4$ solution. The statistical relevance of the independent variables at 0.62 and 1.73 are significantly below the values for control significance factor. However, the corresponding percentage significance values are 7.09% and 23.86% which shows exposure time is slightly relevant to a minimal degree. Nevertheless, the results show SD performance on 1060A is generally independent on inhibitor concentration and exposure time.

**Table 1.** Analysis of variance for SD inhibition performance on AS316 in 3M HCl solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Significance Factor $F$ (Mean Square Ratio) | Control Significance Factor $F$(Min. MSR at 95% confidence) | F (%) |
|---------------------|----------------|------------------|-------------|---------------------------------------------|-------------------------------------------------|-------|
| SD concentration    | 48390.65       | 5                | 9678.13     | 10.52                                       | 2.53                                            | 111.04|
| Exposure Time       | 32411.26       | 6                | -5401.88    | -5.87                                       | 2.42                                            | -74.37|
| Residual            | 27602.05       | 30               | 920.07      |                                             |                                                 |       |
| Total               | 43581.44       | 41               |             |                                             |                                                 |       |

**Table 2.** Analysis of variance for SD inhibition performance on MS in 1M HCl solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Significance Factor $F$ (Mean Square Ratio) | Control Significance Factor $F$(Min. MSR at 95% confidence) | F (%) |
|---------------------|----------------|------------------|-------------|---------------------------------------------|-------------------------------------------------|-------|
| SD concentration    | 137332.96      | 5                | 27466.59    | 7.76                                        | 2.53                                            | 45.22 |
| Exposure Time       | 60272.37       | 6                | 10045.39    | 2.84                                        | 2.42                                            | 19.84 |
| Residual            | 106125.08      | 30               | 3537.50     |                                             |                                                 |       |
| Total               | 303730.39      | 41               |             |                                             |                                                 |       |

**Table 3.** Analysis of variance for SD inhibition performance on 1060A in 2M H$_2$SO$_4$ solution at 95% confidence level

| Source of Variation | Sum of Squares | Degree of Freedom | Mean Square | Significance Factor $F$ (Mean Square Ratio) | Control Significance Factor $F$(Min. MSR at 95% confidence) | F (%) |
|---------------------|----------------|------------------|-------------|---------------------------------------------|-------------------------------------------------|-------|
| SD concentration    | 17903.23       | 5                | 3580.65     | 0.62                                        | 2.53                                            | 7.09  |
| Exposure Time       | 60221.84       | 6                | 10036.97    | 1.73                                        | 2.42                                            | 23.86 |
| Residual            | 174238.57      | 30               | 5807.95     |                                             |                                                 |       |
| Total               | 252363.64      | 41               |             |                                             |                                                 |       |
Adsorption isotherm studies

Adsorption of SD corrosion inhibitor on the metallic surfaces was studied through the use of mathematical models known as adsorption isotherms [14]. Langmuir, Frumkin and Freundlich isotherms shown from Figures 4(a) to 7(b) produced the best fits among the isotherms tested with correlation coefficients above 0.9991. Frumkin isotherm states that the surface coverage depends on the potential of the metal surface due to variation in the energy of the double-layer capacitor. The Frumkin equation is shown below;

\[
\log \left[ C_{SD} \times \frac{\theta}{1 - \theta} \right] = 2.303 \log K_{ads} + 2\alpha \theta
\]  

The Langmuir isotherm that (i) constant interfacial surface reaction, (ii) the extent of inhibitor coverage has no effect on Gibbs free energy values and (iii) the effect of lateral interaction resulting from the molecular reaction of adsorbates on the value of Gibbs free energy is negligible The Langmuir equation is shown below [15].

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

Freundlich isotherm focuses the relationship between adsorbed inhibitor SD molecules, their lateral interaction effect and the mechanism of adsorption [16]. The Freundlich equation is as follows;

\[
\theta = K C^n
\]

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

n is a constant with respect to the characteristics of adsorbed MTH molecule, \( K_{ads} \) is the adsorption-desorption equilibrium constant representing the intermolecular strength of the adsorbed layer.

Figure 4 Langmuir isotherm plots of (a) SD adsorption on AS316 and (b) SD adsorption on 1060A
Figure 5. Langmuir isotherm plots of (a) SD adsorption on AS316 and (b) SD adsorption on 1060A.

Figure 6. Frumkin isotherm plots of (a) SD adsorption on AS316 and (b) SD adsorption on MS and (c) SD adsorption on 1060A.
4. CONCLUSION

2-mercaptobenzothiazole effectively inhibited the corrosion of 316 austenitic stainless steel in HCl and 1060 aluminium alloy in H₂SO₄ solution respectively. However, the inhibitor compound performed poorly on mild steel with average inhibition performance below 60%. Data from statistical analysis shows independent variables of inhibitor concentration and exposure time influenced the inhibition performance of 2-mercaptobenzothiazole at varying degrees due to the specific interaction mode of the inhibitor with the metal surface. Data from adsorption isotherm showed that Langmuir, Frumkin and Freudlich isotherms produced the best fits with correlation coefficient close to unity.

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REFERENCES

[1]. Uhlig HH 1962. The importance of corrosion research. Corrosion 18(9):311t–315t.
[2]. Loto RT 2017. Study of the corrosion behaviour of S32101 duplex and 410 martensitic stainless steel for application in oil refinery distillation systems. J. Mater. Res. Technol. 6(3):203–212.
[3]. Hashimoto K, Asami K, Kawashima A, Habazaki H and Akiyama E 2007. The role of corrosion-resistant alloying elements in passivity. Corros. Sci. 49(1):42–52.
[4]. Singh DK, Kumar S, Udayabhanu G and John RP. 2016. 4(N,N-dimethylamino) benzaldehyde nicotinic hydrazone as corrosion inhibitor for mild steel in 1 M HCl solution: An experimental and theoretical study. J. Mol. Liq. 216:738-746.
[5]. Raja PB and Sethuraman MG 2008. Natural products as corrosion inhibitor for metals in
corrosive media — *A review*. *Mat. Letts.* **62**(1):113-116.

[6]. Loto RT and Babalola P 2017. Corrosion polarization behavior and microstructural analysis of AA1070 aluminium silicon carbide matrix composites in acid chloride concentrations. *Cogent Eng.* 4:1422229. [https://doi.org/10.1080/23311916.2017.1422229](https://doi.org/10.1080/23311916.2017.1422229).

[7]. Loto RT 2018. Investigation of the localized corrosion resistance of 4044 aluminum alloy in acid chloride and neutral chloride solutions. *J. Fail. Anal. Prev.* 18:905–911. [https://doi.org/10.1007/s11668-018-0474-9](https://doi.org/10.1007/s11668-018-0474-9).

[8]. Davis JR 1999. Corrosion of aluminum and aluminum alloys, *Materials Park*, OH. ASM International.

[9]. Hays GF 2010. Now is the Time. *World Corrosion Organization*, New York.

[10]. Hou X, Gao L, Cui Z and Yin J 2018. Corrosion and protection of metal in the seawater desalination. *IOP Conf. Ser.: Earth Environ. Sci.* 108:022037.

[11]. Hansson CM 2011. The impact of corrosion on society. *Metall. Mater. Trans.* A. 42:2952–62.

[12]. Papavinasam S, Doiron A, Panneerselvam T and Revie RW 2007. Effect of hydrocarbons on the internal corrosion of oil and gas pipelines. *Corrosion*. **63**:704–712.

[13]. Loto RT 2019. Corrosion inhibition effect of non-toxic α-amino acid compound on high carbon steel in low molar concentration of hydrochloric acid. *J. Mater. Res. Techn.* **8**(1):484-493.

[14]. Bulut E, Ozacarand M, Sengil IA 2008. Adsorption of malachite green onto bentonite: Equilibrium and kinetic studies and process design. *Micropor. Mesopor. MAT.* **115** (2008) 234–246.

[15]. Guidelli R 1992. Adsorption of molecules at metal electrodes, Kowski, J.L., Ross, P.N (eds.), VCH Publishers, Inc., New York, p.1.

[16]. Ashish KS and Quraishi MA 2011. Investigation of the effect of disulfiram on corrosion of mild steel in hydrochloric acid solution. *Corros. Sci.* **53**(4):1288-1297