Corrosion inhibition of low carbon steel in HCl by 2-mercapto-5-(2-methoxyethyl)amino-1,3,4-thiadiazole: insights from gravimetric analysis and SEM

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Abstract

The anti-corrosion properties of 2-mercapto-5-(2-methoxyethyl)amino-1,3,4-thiadiazole (MMAT) for low carbon steel in 1 M HCl was investigated by weight loss measurements and scanning electron microscopy (SEM). As part of the evaluation of performance, the study focused on different parameters that influenced corrosion inhibition such as concentration of MMAT, time of immersion and temperature. The highest inhibition efficiency obtained was on 92.2% at the 0.5 mM MMAT concentration and at the 303 K temperature thus definitively proving the efficiency of the used inhibitor. From the gravimetric analysis it was evidenced that inhibition efficiency increased with increasing immersion time and temperature. A rise of efficiency with temperature and as supported by $\Delta G_{\rm ads}^0$ values calculated for the reaction that occurred showed that MMAT exhibits both the physical and chemical adsorption on the surface of the steel. The adsorption process can be explained in terms of the Langmuir adsorption isotherm and experimental data backed the process. Based on the SEM analysis, it was established that the formation of MMAT led to the development of a barrier on the surface of steel thus preventing corrosion. This study helps to understand the particulars of MMAT's corrosion inhibition mechanism because of the detailed examination of these parameters. This research contributes positively to the knowledge of MMAT's mode of operation in preventing corrosion in acidic environments for future reference. It can be concluded that MMAT is the suitable candidate for further elaboration of corrosion inhibitors, which could be used in different branches of industry where the metal protection is an essential factor.

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1. Introduction

The study of corrosion inhibition is important as it helps in preventing degradation of material making it a bearing solution [1, 2]. Low carbon steel commonly applied in the numerous sectors of industry is known to have high corrosion susceptibilities particularly in acidic conditions. Thus, to enhance the durability of the used materials and keep the efficiency of various equipment and structures under industrial conditions, it is necessary to create sound corrosion inhibition techniques relying on the presence of acids in various processes [3, 4]. Organic inhibitors are slightly different and are more friendly to the environment than the inorganic inhibitors; they have high efficiency rates and versatility, though their efficiency is sometimes determined by some things like chemical structures and environments in use [6-10]. Extensive literature has been previously published on the design of potent inhibitors that incorporated heteroatoms which include oxygen, nitrogen and sulfur and functional groups that include triple bond, conjugated double bond as well as aromatic ring. From the chemical formula mentioned above, it can be noted that the compound is containing sulfur, oxygen and nitrogen, one of them is named 2-mercapto-5-(2methoxyethyl)amino-1,3,4-thiadiazole (MMAT). MMAT can interact with metals through the abovementioned heteroatoms; these interact with the d-orbitals of metals which makes MMAT a prospective candidate for corrosion inhibition. However, due to the more intricate structure of MMAT, it may reduce the inhibition performance, which should be further studied.

Research conducted in 2022 was concerned with the study of corrosion inhibition of low carbon steel (LCS) in hydrochloric acid employing heterocyclic derivatives. Concretely, the potentiodynamic polarization assessment analyzed the efficiency of the test heterocyclic compound in HCl solutions and proved the tested compound to be a corrosion inhibitor. Also, in the same year, a study was conducted to estimate on the effectiveness of bisbenzothiazole derivatives as hetero cyclic compound in the inhibition of low carbon steel corrosion in 1 M HCl. This research accord considerable knowledge about the corrosion inhibition probability of these derivatives and the result revealed that it had a great impact on the low carbon steel in acidic solution [12]. Thus, it could be concluded that the synthesized heterocyclic derivatives give excellent inhibition performance in 1 M HCl environment [13]. A literature review of the same year analyzed the applicability of heterocyclic derivatives as inhibitors for corrosion of steel with HCl solution, hence, expressing the high order anticorrosive properties of the low carbon steel inhibitors in giving protection to HCl solutions [14]. In 2023, there was a research that looked at the potential of a new oxazole derivative for application as a corrosion inhibitor on Low Carbon Steel in 0.5 M hydrochloric acid. The role of this research was to establish the ability of the compound to reduce HCl corrosion, which was discovered in the study [15]. Moreover,

another work published in the same year looked at the effectiveness of new designed azole analogues in the corrosion inhibition of low carbon steel in 1 M HCl solution. It was established that these derivatives may be useful as corrosion inhibitors through the studies revealed [16]. The cumulative results of these investigations are directed toward the capability of azole derivatives in protecting from corrosive attack in acidic solutions. The compound studied in this research, 2-mercapto-5-(2-methoxyethyl)amino-1,3,4-thiadiazole (MMAT), contains both azole and amino-groups, which would collectively improve this compound's ability to inhibit corrosion as compared to individual compounds in the material. However, the comprehensible knowledge about corrosion inhibitors as well as the new compounds is still rather limited. In their works, scholars have also examined numerous corrosion inhibitors and have also pointed out potential uses for the substances, as well as the ways for the optimization of the inhibitors' efficiency. The research work annoys a new perspective by evaluating the efficiency of the corrosion inhibitor MMAT on low carbon steel in HCl solution. Compared to past studies isolated different organic and inorganic inhibitors, this study integrates gravimetric analysis and SEM to evaluate the entire manner of corrosion inhibition of MMAT. The presence of both an azole and an amine moiety, both of which are well-documented corrosion inhibitors, may exhibit an additive or even mutually enhancing effect, to the best of the authors' knowledge. The purpose of this research is to assess the inhibition efficiency of MMAT (Figure 1) on low carbon steel in HCl concentration. To this end, one is able to identify the effect of the different parameters including the concentration of MMAT, immersion time as well as temperature on the corrosion inhibition efficiency. The main objectives of the current work can be summarized as follows:

- 1. To evaluate the effectiveness of the corrosion inhibition performed by MMAT on low carbon steel in 1.0 M HCl environment using gravimetric techniques.
- 2. Analyze how MMAT concentrations influence the corrosion inhibition efficiency.
- 3. Investigate the effects of various immersion periods on the efficiency MMAT as a corrosion inhibitor.
- 4. Investigate the effect of temperature with the percentage of inhibition efficiency of MMAT.
- 5. To use scanning electron microscopy (SEM) to analyze the surface morphology of low carbon steel after treatment with MMAT, providing visual evidence of corrosion inhibition.
- 6. To investigate the adsorption behavior of MMAT on the metal surface and determine the adsorption isotherms and thermodynamic parameters, providing insights into the mechanism of inhibition.
- 7. To elucidate the corrosion inhibition mechanism of MMAT by combining experimental data with SEM technique, enhancing the understanding of its protective effects.

8. To provide valuable information that can aid in the development of effective corrosion mitigation strategies for industrial applications involving low carbon steel in acidic environments.

Figure 1. Chemical structure of MMAT.

2. Experimental Techniques

2.1. Materials and sample preparation

Low carbon steel coupons, supplied by Metal Samples Company, were used as working electrodes. The chemical composition of the low carbon steel, by weight percentage, is provided in Table 1. Preparation of the low carbon steel coupons followed the standard cleaning procedures as outlined in ASTM G1-03 [17].

Table 1. Chemical co	mposition of low	carbon steel coupo	on (wt.%).
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Number	Element	Percentage, %
1	Carbon	21
2	Manganese	5
3	Silicon	3.8
4	Aluminum	1
5	Sulfur	5
6	Phosphorus	9
7	Iron	Balance

2.2. Acid medium

Acid used in the tests was prepared by diluting analytical reagent-grade 1 M hydrochloric acid (37%) with double-distilled water.

2.3. Weight loss measurements

Weight loss measurements were done in 1 M HCl, both with and without the corrosion inhibitor, using low carbon steel samples with dimensions $45 \times 25 \times 0.2$ mm. The steel samples were sanded with sandpaper up to 1200 grit, weighed, and immersed in 100 mL of 1 M HCl in a 250 mL beaker. Inhibition efficiency was assessed at different concentrations of the

inhibitor, specifically at 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, 0.5 mM, and 1 mM. After immersion times of 1, 5, 10, 24, and 48 h, the steel samples were rinsed with water (double-distilled) and used acetone for cleaning and dried in an oven, and finally reweighed. The corrosion rate (C_R ; mm/y) and inhibition efficiency (IE%) were calculated using Equations (1) and (2) [18–20]:

$$C_{\rm R} = \frac{87.6(W_{\rm initial} - W_{\rm final})}{A \cdot t} \tag{1}$$

$$IE = \frac{87.6(W_{\text{initial}} - W_{\text{final}})}{A \cdot t} \cdot 100 \tag{2}$$

where C_R is the corrosion rate, 87.6 is a constant convert the corrosion rate between the mils per year and the metric equivalent millimeter per year, W_{initial} is he initial weight of the sample before immersion in the corrosive solution, measured in grams (g), W_{final} is the final weight of the sample after immersion in the corrosive solution, measured in grams (g), A is the surface area of the sample exposed to the corrosive environment, measured in square centimeters (cm²), and t is the time duration of exposure, measured in hours (h).

Weight loss tests reproducibility was confirmed under controlled conditions by testing three trials.

2.4. Effect of temperature

Temperature dependent tests were performed at 303, 313, 323, and 333 K using LCS samples of selected thickness. Each test involved immersing the coupons in 100 mL of 1 M HCl in a 250 mL beaker for 5 hours. Post-exposure, the coupons were processed as described previously. All experiments were repeated three times to ensure consistency [20].

2.5. Adsorption isotherms

The inhibitor molecules adsorption behavior was studied to gain insights into their characteristics. Surface coverage (θ) values for different inhibitor concentrations were determined from weight loss measurements using a scale with a sensitivity of 0.001 g. Various adsorption isotherms, including Langmuir, Freundlich, and Temkin, were applied to analyze the data [21].

Langmuir isotherm equation:
$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C$$
 (3)

Temkin isotherm equation:
$$\theta = \frac{-\ln K_{\text{ads}}}{2a} - \frac{\ln C}{2a}$$
 (4)

Frumkin isotherm equation:
$$\ln \frac{\theta}{1-\theta} = \ln K_{\text{ads}} + 2a$$
 (5)

where θ is the surface coverage degree, C is the inhibitor concentration, and K_{ads} is a constant for the adsorption.

2.6. SEM analysis

Low carbon steel samples were immersed in both uninhibited and inhibited solutions for 5 hours to assess the impact of MMAT on surface morphology. The samples were then analyzed using a Compact Field Emission Scanning Electron Microscope (FESEM), specifically the Zeiss MERLIN, at a resolution of 0.8 nm (15 kV/1.6) in STEM mode. These observations were conducted at the Electron Microscopy Unit of Universiti Kebangsaan Malaysia in Selangor. Post-immersion, the steel coupons were thoroughly rinsed with distilled water, dried, and subjected to SEM analysis.

3. Results and Discussion

3.1. Gravimetrical measurements

3.1.1. Effect of concentration

The study investigates the impact of different concentrations of the corrosion inhibitor, 2-mercapto-5-(2-methoxyethyl)amino-1,3,4-thiadiazole (MMAT), on the corrosion rate (C_R) and inhibition efficiency (IE%) of low carbon steel in 1 M HCl solution after 5 hours of immersion. The concentrations examined were 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, 0.5 mM, and 1 mM. The following analysis highlights the observed trends and provides insights into the inhibitor's performance at these varying concentrations (Figure 2).

The corrosion rate is a critical parameter that quantifies the metal's degradation over time. The data clearly indicates a decrease in corrosion rate with increasing concentrations of MMAT. This trend suggests that higher concentrations of MMAT are more effective in reducing the corrosion rate of low carbon steel in acidic environments. The most significant reduction is observed between 0.1 mM and 0.5 mM, where the corrosion rate drops from 1.06 mm/y to 0.33 mm/y. At 1 mM, the corrosion rate slightly decreases further to 0.32 mm/y, indicating that the inhibitor's effectiveness reaches a near plateau at higher concentrations. Inhibition efficiency measures the percentage reduction in corrosion rate due to the presence of the inhibitor. The inhibition efficiency shows a marked improvement with increasing inhibitor concentration. At 0.1 mM, the inhibitor achieves an *IE*% of 41.5%, indicating a moderate reduction in corrosion rate. However, as the concentration increases to 0.2 mM and 0.3 mM, the inhibition efficiency rises significantly to 64.5% and 75.8%, respectively. This substantial increase highlights the enhanced protective effect of MMAT at these concentrations.

Further increases in concentration to 0.4 mM and 0.5 mM result in even higher inhibition efficiencies of 83.8% and 92.2%, respectively. At 1 mM, the *IE*% slightly improves to 94.1%, indicating that the inhibitor's performance is nearing its maximum potential. This plateau suggests that beyond 0.5 mM, additional increments in concentration yield diminishing returns in inhibition efficiency.

The analysis demonstrates that MMAT is highly effective in reducing the corrosion rate of low carbon steel in 1 M HCl solution. The observed trend of decreasing corrosion rate

and increasing inhibition efficiency with higher concentrations of MMAT indicates a strong correlation between inhibitor concentration and its protective capability.

- At lower concentrations (0.1 mM to 0.2 mM): There is a significant reduction in corrosion rate and a corresponding increase in inhibition efficiency. This indicates that even at relatively low concentrations, MMAT can provide substantial protection against corrosion.
- At moderate concentrations (0.3 mM to 0.5 mM): The inhibition efficiency continues to increase, reaching over 90% at 0.5 mM. This suggests that MMAT forms a more effective protective layer at these concentrations, further reducing the metal's exposure to the corrosive environment.
- At higher concentration (1 mM): The inhibition efficiency increases marginally compared to 0.5 mM, indicating that the inhibitor's performance is nearing its maximum. This plateau effect suggests that the adsorption sites on the metal surface are nearly saturated at this concentration.

Overall, the data suggests that MMAT is an effective corrosion inhibitor for low carbon steel in acidic environments, with optimal performance observed at concentrations around 0.5 mM. Beyond this concentration, the improvement in inhibition efficiency is minimal, indicating a saturation point for the inhibitor's effectiveness. Future studies could explore the long-term stability and performance of MMAT at these optimal concentrations, as well as investigate the inhibitor's performance under varying environmental conditions and in the presence of different corrosive agents.

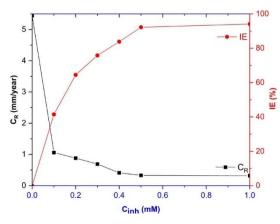


Figure 2. Effects of C_R and IE% for LCS samples immersed for 5 h., in a 1 M HCl solution at 303 K, tested across different MMAT concentrations.

The enhancement of the corrosion inhibition efficiency with the increase in MMAT concentration can be as a result of several characteristics related to MMAT molecular structure. The aromatic groups of MMAT raise the electron density at active sites which in turn lead to a higher interaction between the MMAT molecules and the active metal surface-Fe iron atoms. Furthermore, nitrogen, oxygen, and sulfur within MMAT create coordination between these atoms and the metal surface to improve adsorption and to provide an anti-

corrosive layer. However, it is necessary to state that depending on the selected corrosion inhibitor concentration, the corrosion of low carbon steel in 1 M HCl can be different. Although it is found that, the increasing the concentration of the inhibitors exhibits more effective corrosion protection, in practice, it is observed that the concentration of the inhibitor varies with the type and grade of the inhibitor, temperature of the solution and the presence of other ions in the solution. Some inhibitors may reduce the frequency of the attack or corrosion incident at lower concentrations and but may perform poorly or even become corrosive at higher concentrations [22, 23]. Different investigation has explored the various inhibitor concentrations effect on C_R of LCS in 1 M HCl. For example, Fang investigated different organic corrosion inhibitors in an acidic environment and found that higher concentration resulted in lower C_R , although this differences depending on the type of inhibitor. Likewise, studies on natural inhibitors, such as pomegranate peel extract and castor oil, have shown a concentration-dependent reduction in corrosion rate, with optimal concentrations resulting in peak inhibition efficiency [24, 25].

This trend suggests that there exists an optimal concentration range for the inhibitor (around 0.5 mM) where corrosion rate reduction and inhibition efficiency are maximized. Increasing the concentration beyond this point may not yield substantial additional benefits in terms of corrosion inhibition. Additionally, it's essential to consider practical factors such as cost-effectiveness and potential side effects of higher inhibitor concentrations when determining the optimal concentration for real-world applications.

3.1.2. Effect of immersion periods

Based on the data from Figure 3, the impact of inhibitor concentration on corrosion rate (C_R) and inhibition efficiency (IE) at different exposure times (1 hour, 5 hours, 10 hours, 24 hours, and 48 hours) can be discussed as follows:

a. Corrosion Rate (C_R) :

- With the rise in inhibitor concentration from 0.1 mM to 1.0 mM, the corrosion rate is reduced progressively at all exposure periods.
- The maximum corrosion rates are obtained at the lowest inhibitor concentration which is 0.1 mM while gradually as the concentration of the inhibitor is increased the corrosion rates steadily reduce.
- As can be observed at each of the exposure time, the corrosion rate reduces with increase in the concentration of the inhibitor hence confirming the efficiency of the inhibitor in the reduction of corrosion over time.

b. Inhibition Efficiency (*IE*):

- Likewise, the inhibition efficiency rises as the inhibitor content has been raised as well.
- At 0.1 mM inhibitor concentration the inhibition varies from 38.9% to 64.3% depending with the exposure time.

- Wang and Li also observe that there is a direct relation between the inhibitor concentration and the inhibition efficiency. At this concentration, inhibition efficiencies are in the range of 82.5% to 97.3% for all the extracts tested.
- The greatest values of inhibition efficiencies are obtained at the greatest value of inhibitor concentration (1 mM), and exposure time, suggesting that the levels of effectiveness of the inhibitor increase as the duration of the corrosion process progresses.

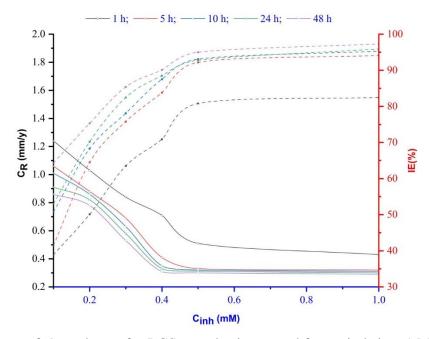


Figure 3. Effects of C_R and IE% for LCS samples immersed for periods in a 1 M HCl solution at 303 K, tested across different MMAT concentrations.

The changes of the values of inhibitor concentration, corrosion rate reduction and inhibition efficiency are summarized in the data above. Thus, higher inhibitor concentration cause lower corrosion rate and higher inhibition efficiency showing the efficiency of the inhibitor in the protection from corrosion. Also, overall, the inhibition efficiency increases with higher exposure time, further confirming the ability of the inhibitor to protect metal surface for a longer period [26].

The effectiveness of MMAT and immersion duration escalates progressively; this shows MMAT to be more reliable than mere corrosion inhibitors for metal surface protection against corrosion. Thus, MMAT's inhibitory efficiency has proven to be highly dependent on the metal substrates and has slowly increasing tendencies within the first 10 to 48 hours of immersion. This improvement is as a result of enhancement in adsorption of MMAT molecules on the metal substrate due to the catalytic nature of the metal [27]. Thus, due to the formation of a uniform layer of MMAT molecules on the surface of the protected material, the effectiveness of inhibitors is increased and corrosion is prevented [28,29]. The inhibitory mechanism of MMAT is not very clear and is refined by different factors such as

temperature, pH, and concentration of the solution in which it is used and thus require close control. Interestingly, there is perfect hydrogen bonding as well as coordination interactions that exist between MMAT and the metal substrate and therefore makes MMAT quite efficient corrosion inhibitor for metal in acidic media. Due to the high adsorption density of MMAT both physisorption and chemisorption are possible and the MMAT layer becomes even stronger protecting the substrate and raising the inhibitory performance [30]. The ratting inhibitory effectiveness of MMAT over rather long exposure timeframe warrants the compound as a corrosion inhibitor, as well as proclaims its utility in conferring durable protection of metal against corroding agencies, and hence the commodity's role in surface protection.

3.1.3. Effect of temperature

Temperature has a significant influence on the intensity of the destructive environment and the relations of low carbon steel surfaces with such inhibitors as MMAT. Temperature was studied with respect to gravimetric measurements carried out in 1 M HCl solution with different concentration of MMAT (Figure 4).

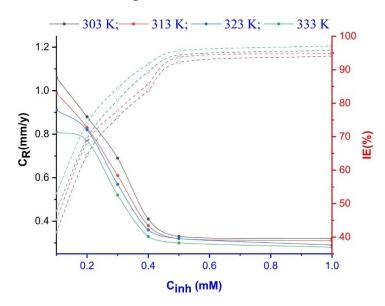


Figure 4. Effects of C_R and IE% for LCS samples immersed for 5 h., period in a 1 M HCl solution at 303–333 K, tested across different MMAT concentrations.

Our data revealed a consistent trend: as temperature increased, the corrosion rate noticeably decreased in the presence of different inhibitor concentrations over a 5-hour immersion period [31, 32]. This suggests that higher temperatures contribute to reducing corrosive activity on low carbon steel surfaces, particularly with MMAT molecules. Additionally, surface coverage (θ), determined by the ratio of inhibition efficiency (IE) to 100, exhibited a slight increase with rising temperature in the presence of MMAT. This means that, at high temperatures, there would be better adsorption of the MMAT molecules on the LCS surfaces. However, the slight improvement of surface coverage indicate that the protective ability of MMAT is relatively insensitive to the temperature change of working

environment in the range of this research [33, 34]. Consider this scenario: Thus, at 303 K, the corrosion rate with MMAT might be 0. At 343 K, it is 5 mm/year while at 333 K, the increase is reduced to 0.3 mm/year. This means corrosion rate decreases with the increase in temperature and this is the virtue of MMAT compound because, higher temperatures promote adsorption and Film forming characteristics of MMAT molecules [35]. In conclusion, the data presented herein allow it to be stated that MMAT can be considered as an effective inhibitor when exposed to emission tested within the entire range of investigated temperature characteristics and the deterioration of its protective characteristics is rather minimal despite its exposure to temperature variations. This temperature stability puts MMAT in a good stand as a consistent corrosion inhibitor regardless of the changing environmental conditions thus increasing its practicality in the anti-corrosion deliberations for low carbon steel.

However, more research could be conducted to allow a deeper understanding of the factors or processes through which temperature influences corrosion inhibition or the effectiveness of inhibitors in real-world applications. From the experimental data shown in Figure 4, a general tendency of the corrosion rate of low carbon steel to decrease with increasing temperature can be identified and believed that the corrosion process is subject to certain reaction kinetics and thermodynamics. Chiefly, temperature plays a very crucial role in terms of making the reaction faster or slower. Usually if the temperatures get high the rate of chemical reactions increases because of higher kinetic energy of the reacting molecules. In the context of corrosion protection, the increased kinetic energy is beneficial since it allows inhibitors to rapidly adsorb onto metal interfaces. As a result, there are more availability sites on the metal surface for the inhibitor molecules to adhere to and to form a layer that is thicker and more "compact" as a barrier to the corrosive species. Moreover, temperature variations affect the thermodynamics of the corrosion process. Typically, elevated temperatures enhance chemical particles dissolution and reactants diffusion, impacting overall C_R . With MMAT, the using of high temperature may promote thermodynamic favorability of inhibitor adsorption onto LCS surface. This, coupled with accelerated reaction kinetics, led to more efficient corrosion inhibition with higher temperatures. Moreover, temperature affects the reactivity and stability corrosion products formed on LCS surface. At raised temperature, the composition and structure of corrosion products may vary, that could alter their protective characteristics and thus the overall corrosion rate of the metal.

Based on the data from Figure 4, we can observe the effect of inhibitor concentration on the C_R and IE at different temperatures (303 K, 313 K, 323 K, and 333 K):

a. Corrosion Rate (C_R) :

• For all inhibitor concentrations (0.1 mM to 0.5 mM), the corrosion rate decreases as the temperature increases. This trend is consistent across all concentrations and temperature intervals.

- At each temperature, higher inhibitor concentrations correspond to lower corrosion rates. For instance, at 303 K, the corrosion rate decreases from 1.06 mm/y at 0.1 mM to 0.33 mm/y at 0.5 mM.
- The impact of temperature on corrosion rate reduction is more pronounced at higher inhibitor concentrations. For example, at 0.5 mM, the corrosion rate decreases from 0.33 mm/y at 303 K to 0.3 mm/y at 333 K.

b. Inhibition Efficiency (IE):

- In all cases, it is observed that with an increase in the temperature of the system, there was an increase in inhibition efficiency.
- Concentration of inhibitor increases with increase in inhibition efficiency at each of the applied temperature. For example, at 303 K, inhibition efficiency ranges from 41.5% at 0.1 mM to 92.2% at 0.5 mM.
- Temperature has a greater impact on inhibition efficiency making at higher concentration of the inhibitor. For instance, at 0.5 mM, inhibition efficiency increases from 92.2% at 303 K to 95.7% at 333 K.

In general, the findings of this study indicate that increasing the temperature will improve MMAT performance for the inhibition of corrosion of low carbon steel in HCl. This is clearly estimated by the gradual descent of the corrosion rate and concurrently, the ascent of the inhibition efficiency at higher temperatures of the electrolyte for all investigated inhibitor concentrations. The findings presented in the work may be a valuable source of knowledge regarding the effects of temperature on inhibitors' efficiency and the prospects of MMAT use for corrosion protection when temperature changes are possible, including both, increase and decrease.

3.2. Adsorption isotherm

Hence, the detailed analysis of the relationships between the inhibitor molecules and the metal surface is vital in the determination of corrosion inhibition mechanism. In this survey, θ values were calculated at different inhibitor concentrations to overcome the information on the interactions as follows: Based on the data, two popular isotherm adsorption models, namely Temkin and Langmuir models, were applied here [36, 37]. The data from the gravimetric measurement were then tried to be fitted to various adsorption isotherms and it was observed that Langmuir model fits the experimental findings most accurately. Regarding Langmuir adsorption model, the tested inhibitor concentration (C_{inh}) in acidic medium is related to the θ based on relation (3). C_{inh}/θ and C_{inh} yielded an R^2 (Linear regression) value of 0.993, as demonstrated in Figure 5. Figure 5 illustrates the linear relationship between C_{inh}/θ and C_{inh} at 303 K, validating the adherence of MMAT molecule adsorption on the LCS surface to Langmuir isotherm. However, the deviation of the slope of the plot from unity suggests non-ideal behavior, possibly arising from interactions among the adsorbed MMAT molecules on the metal surface [38, 39].

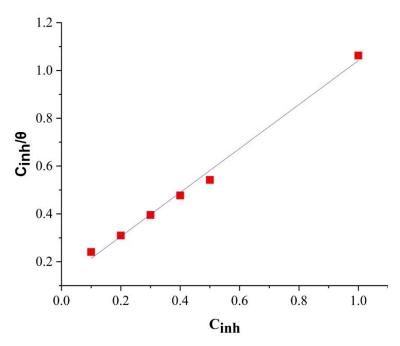


Figure 5. Langmuir model for MMAT molecules adsorption of in acid solution on LCS surface.

Furthermore, we determined the adsorption free energy ($\Delta G_{\rm ads}^0$) and $K_{\rm ads}$ using Equation (6):

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5K_{\text{ads}}) \tag{6}$$

Here, 55.5 is the concentration of water (mol/L), and R is the constant of gas.

Usually, value of about -20 kJ/mol or less for a $\Delta G_{\rm ads}^0$ refers to physical absorption, whereas the values of about -40 kJ/mol or higher indicate chemical absorption. Current investigation the value of $\Delta G_{\rm ads}^0$ was -36.6 kJ/mol indicates the adsorption mechanism involving both chemical and physical interactions between MMAT and LCS in a 1 M HCl solution at 303 K. $\Delta G_{\rm ads}^0$ negative value refers to inhibitor molecules adsorption on the LCS surface is a spontaneous process [40, 41].

3.3. SEM analysis

The SEM analysis aimed to elucidate the surface morphology changes of low carbon steel after immersion in a 1.0 M HCl solution, both without (Figure 6a) and with (Figure 6b) 0.5 mM MMAT for 5 hours at 303 K. In the absence of MMAT, the SEM images reveal significant surface damage due to the aggressive dissolution of iron in the acidic environment. The steel surface appears heavily corroded, with extensive pitting and roughness indicating severe material degradation. In sharp contrast, however, the presence of MMAT radically changes the surface condition. As shown in the SEM image, there is a thin and uniform protective layer on the steel surface, which is evidence of successful MMAT adsorption. This film provides a barrier that will significantly mitigate the corrosive

effects of the medium. The protective film, although there are some cracks that may have been caused by dehydration during sample preparation, effectively insulates the steel from further corrosion. This observation strongly points to the fact that MMAT is a potential corrosion inhibitor, forming a stable and adherent layer that protects the metal surface in acidic environments. From SEM analysis, there is convincing visual evidence to support the effectiveness of MMAT as a corrosion inhibitor for low-carbon steel in an acidic environment. The stark contrast between a severely corroded surface in the absence of MMAT and a relatively intact surface with a protective layer in its presence suggests that there could be significant protection available from MMAT.

The formation of a uniform, adherent layer by MMAT indicates that its adsorption onto the steel surface is strong, likely involving physical and chemical interactions. The presence of heteroatoms such as nitrogen and sulfur in MMAT facilitates the complexation process with iron atoms, providing better stability and effectiveness of the protective layer. It demonstrates the dual role of MMAT in corrosion inhibition. It is the dense film that makes up MMAT, which can withstand harsh acidic conditions, and functions in two different modes: first, physically by acting as a barrier; Secondly, chemically by reacting with the metal surface to form a stable protective compound. Noticeable cracks in the protective layer, which can be attributed to dehydration during the drying process, give the feeling that although very effective in forming an initial barrier, further improvement in the inhibitor formulation or application process may be needed to enhance the integrity and durability of the layer. This requires modification of the drying protocol or addition of supplementary agents aimed at improving film consistency and flexibility. The SEM results are, in general, consistent with the results obtained from weight loss and gravimetric methods, confirming that MMAT is an excellent corrosion inhibitor. It may find useful applications in the industrial sector where low carbon steels are exposed under acidic conditions, thus replacing other commonly used corrosion inhibitors. Further studies need to be conducted on the longterm stability of the MMAT film, its performance under different environmental conditions, and its compatibility with other corrosion prevention methods in order to realize its full potential for a corrosion protection strategy.

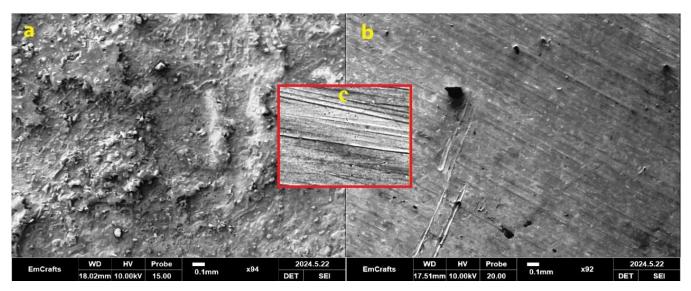


Figure 6. SEM micrographs of low carbon steel at 303 K (a) in 1.0 M HCl solution in the absence of MMAT, (b) in 1.0 M HCl solution in presence of MMAT and (c) initial SEM micrograph in absence of MMAT.

3.4. Suggested inhibition mechanism

The inhibition mechanism of MMAT in HCl solution is a multistep process driven by the interaction between MMAT molecules and the metal surface. Based on experimental observations and SEM considerations, we propose the following mechanism [42–44]:

- 1. MMAT molecules adhere to the LCS surface through electrostatic interactions and chemical bonds. Sulfur and nitrogen atoms within MMAT have the ability to coordinate with the LCS surface, and forming a protective layer through coordination bonds.
- 2. In MMAT molecules, sulfur and nitrogen atoms possess a strong affinity for the Fe atoms d-orbitals on the LCS surface, which form metal complexes, where the molecules of MMAT represent Lewis bases, donating pairs of electrons to Fe atoms d-orbitals, thereby reducing their reactivity.
- 3. Continued adsorption of MMAT molecules leads to the development of a stable and dense protective film that acts as a barrier, preventing acidic species from accessing the LCS surface and impedance corrosion reactions.
- 4. MMAT electron donors are at the core of the electron transfer processes, which occur between inhibitor molecules and the LCS surface. This electron transfer reduces metal ions, thereby inhibiting their dissolution into the HCl environment.
- 5. The MMAT molecule coordinate with other species in the HCl solution, such as Cl ions, would give rise to certain synergistic effects that result in increased inhibitive performance. These complexations further stabilize the protective film and inhibit corrosion.
- 6. The mechanism of inhibition is operative over a wide range of temperatures; however, temperature changes may further affect adsorption kinetics and film

stability. Higher temperatures can elevate the kinetics of adsorption, thereby enhancing the interaction of MMAT molecules with the metal surface and increasing inhibition efficiency.

The mechanism of corrosion inhibition by MMAT is, therefore, intertwined with complex physical and chemical interactions, mainly through the adsorption process. Comprehending this mechanism would be critical to understanding how MMAT reduces corrosion rates effectively in an acid medium. More plausibly, it can be considered that the MMAT molecules get attached to the low carbon steel surface via van der Waal forces, which is a type of physical adsorption. This leads to the formation of a protective layer, which acts as a barrier between the metal substrate and the corrosive acid, hence reducing the rate of corrosion [45–48].

Moreover, MMAT shows a certain degree of chemical reactivity with the corrosion byproducts on the metal surface, which additionally attenuates corrosion rates. For example, the reaction of MMAT with iron oxides that form on a steel surface forms a protective film, preventing further corrosion from proceeding [49, 50]. Figure 7 shows the different inhibition mechanisms explaining the adsorption process:

- 1. MMAT can undergo chemical adsorption onto the LCS surface by giving pairs of electrons from oxygen, nitrogen and/or sulfur atoms to unequipped d-orbital of Fe atom.
- 2. π -electrons from heterocyclic ring, along with the unoccupied d-orbitals of Fe atom, engage in electronic interactions.

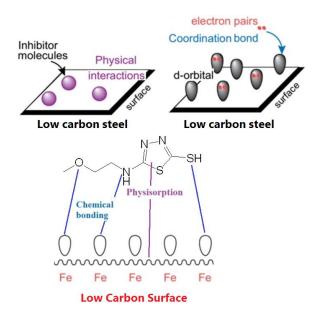


Figure 7. The suggested inhibition mechanism.

4. Conclusion

In summary, the study of 2-mercapto-5-(2-methoxyethyl)amino-1,3,4-thiadiazole as a corrosion inhibitor of low-carbon steel in a 1.0 M HCl solution can provide some useful information regarding its corrosion inhibitor efficiency. Gravimetric measurements and SEM analysis indicate that the compound has remarkable inhibitory efficiency; At a concentration of 0.5 mM and a temperature of 303 K, the inhibition rate reached 92.2%. The trends in inhibitory performance of MMAT were found to be progressive with increasing concentration, immersion time, and temperature. The adsorption isotherm analysis demonstrated that the Langmuir adsorption isotherm model followed the MMAT model, indicating a good interaction between MMAT molecules and the surface of low-carbon steel. The determined adsorption free energy value, -36.6 kJ/mol, indicates that adsorption occurred spontaneously, coupled with chemical and electrostatic interactions. The MMAT inhibition mechanism proposed here is based on physical adsorption through van der Waals interactions and chemical interactions with the metal surface and corrosion products. This will effectively reduce the corrosion rate, thus attesting to the ability of MMAT to act as a corrosion inhibitor in acidic environments. The overall results of this research enrich the existing literature on the corrosion prevention mechanism of MMAT and its potential application as a protective agent on low-carbon steel in acidic medium. Therefore further research can be conducted to achieve long-term stability and practical applications in industries related to MMAT-based corrosion prevention strategy.

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