CHAPTER-IV

SYNTHESIS AND CORROSION INHIBITION CHARACTERISTICS OF OXADIAZOLES DERIVATIVES ON MILD STEEL IN HYDROCHLORIC ACID SOLUTION
4.1. Introduction

1,3,4-Oxadiazole is a heterocyclic compound containing an oxygen atom and two nitrogen atoms in a five-membered ring. It is derived from furan by substitution of two methylene groups (=CH-) with two pyridine type nitrogens (-N=). The replacement of two -CH= groups in furan by two pyridine type nitrogen (-N=) reduces aromaticity of resulting oxadiazole ring to such an extent that the oxadiazole ring exhibit character of conjugated diene. There are three known isomers: 1,2,4-oxadiazole, 1,2,3-oxadiazole and 1,2,5-oxadiazole. However, 1,3,4-oxadiazole and 1,2,4-oxadiazole are better known, and more widely studied by researchers because of their many important chemical and biological properties. Oxadiazole is a very weak base due to the inductive effect of the extra heteroatom.

It has been noticed continuously over the years that interesting biological activities were associated with oxadiazole derivatives [1-5]. In addition to these biological activities, a good number of oxadiazole derivatives were found applications in corrosion inhibition studies. Bouklah et al. studied corrosion inhibition effect and thermodynamic properties of 2, 5-bis(4-methoxyphenyl)-1,3,4-oxadiazole for mild steel (MS) in normal sulfuric acid solution [6]. A quantum chemical study of the corrosion inhibition efficiency of triazole and oxadiazole derivatives for MS in 1 M hydrochloric acid has been studied by Bentiss and coworkers [7]. Bentiss and coworkers synthesized 2,5-bis(4-dimethylaminophenyl)-1,3,4-oxadiazole and 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole and their inhibiting action on the corrosion of MS in 1 M HCl and 0.5 M H₂SO₄ has been investigated [8]. A quantum chemical study on the corrosion inhibition efficiencies of some oxadiazole derivatives in acidic medium have been reported by Ashry et al [9].

AC impedance studies, X-ray photoelectron spectroscopy and density functional theory studies of newly synthesized 3,5-bis(n-pyridyl)-1,2,4-oxadiazoles, namely 3,5-bis(2-pyridyl)-1,2,4-oxadiazole (2-DPOX), 3,5-bis(3-pyridyl)-1,2,4-oxadiazole (3-DPOX) and 3,5-bis(4-pyridyl)-1,2,4-oxadiazole (4-DPOX) on the corrosion of carbon steel in hydrochloric acid solution has been assessed by Outirite and coworkers [10]. The
electrochemical character of brass in natural seawater in the absence and presence of some oxadiazole derivatives, namely 2,5-bis-(4-aminophenyl)-1,3,4-oxadiazole (BAPOD), 2,5-bis-(4-bromophenyl)-1,3,4-oxadiazole (BBPOD), 2,5-diphenyl-1,3,4-oxadiazole (DPOD), and 2,5-bis-(4-nitrophenyl)-1,3,4-oxadiazole (BNPOD) has been investigated by Joseph Raj and Rajendran [11]. The inhibiting effect of a new class of 2,5-disubstituted-1,3,4-oxadiazoles on the corrosion of MS in 1 M HCl and 0.5 M H₂SO₄ has been investigated by Bentiss et al [12]. Udhayakala and coworkers employed quantum chemical calculations for the inhibition efficiency of two substituted 1,3,4-oxadiazoles namely, 2,5-bis(2-pyridyl)-1,3,4-oxadiazole (POX) and 2,5-bis(2-hydroxyphenyl)-1,3,4-oxadiazole(HPOX) on the corrosion of MS [13]. The influence of 2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole (PNOX) and 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (PAOX) on the corrosion of MS in hydrochloric acid has been studied by Mernari et al [14]. Lebrini et al. assessed the corrosion inhibition efficiency of 3,5-bis(n-pyridyl)-1,3,4-oxadiazole on MS in 1 M perchloric acid solution [15].

Synthesis and corrosion inhibiting action of 2-[1,2,4]-triazole-methyl-4-acetyl-5-nitrophenyl-[1,3,4]-oxadiazole (TMANO) on the corrosion of MS in 0.5 M sulphuric acid solution has been investigated by Tao et al [16]. Udhayakala and coworkers employed density functional theory investigations for the adsorption of some oxadiazole derivatives on MS [17]. The correlation between inhibition efficiency and chemical structure of some 2,5-Bis(n-methoxyphenyl)-1,3,4-oxadiazoles on the corrosion of MS has been studied by Bentiss et al [18]. These compounds rich in heteroatoms can be regarded as environmental friendly inhibitors because of their strong chemical activity and low toxicity [19-20]. Thus, in the light of above, the present chapter reports the antioxidant activity and corrosion inhibition behaviour of newly synthesized compounds, 4-(((4-((5-mercapto-1,3,4-oxadiazol-2-yl)methyl)-5-methylthiazol-2-yl)imino)methyl)benzene-1,2-diol (MOMMBD) and 4-(((4-((5-mercapto-1,3,4-oxadiazol-2-yl)methyl)-5-methylthiazol-2-yl)imino)methyl)2,6-dimethoxyphenol (MOMMDP). The synthesized compounds were characterized by FTIR, elemental analyses and ¹H-NMR spectral studies. Antioxidant activity was studied by assaying diphenylpicrylhydrazyl (DPPH), nitric oxide and hydroxyl radicals. Mass loss and electrochemical techniques were used to elucidate the corrosion inhibition mechanism of MOMMBD and MOMMDP on MS in 0.5 M HCl. The thermodynamic activation and adsorption parameters were calculated and discussed.
4.2. Synthesis of inhibitors

4.2.1. Synthesis of 2-(2-amino-5-methylthiazol-4-yl) acetohydrazide (3) [21]

Yield: 74 %. IR (nujol, cm\(^{-1}\)): 3316, 3148 (NH, NH\(_2\)), 2352 (NH\(_2\)). \(^1\)H NMR (CDCl\(_3\), \(\delta\) ppm): 9.02 (s, 1H, NH), 6.86, 6.21 (s, 4H, 2 NH\(_2\)), 3.17 (s, 2H, CO-CH\(_2\)), 2.31 (s, 3H, CH\(_3\)), 2.19 (s, 2H, NH\(_2\)). Anal. Calcd. (%) for C\(_6\)H\(_{10}\)N\(_4\)O: C - 38.70, H - 5.41, N - 30.08. Found (%): C - 38.74, H - 5.44, N - 30.78.

4.2.2. Synthesis of 2-((2-amino-5-methylthiazol-4-yl) methyl) oxadiazole-5-thiol (4) [22]

Yield: 70 %. IR (nujol, cm\(^{-1}\)): 3368 (NH\(_2\)). \(^1\)H NMR (CDCl\(_3\), \(\delta\) ppm): 13.02 (s, 1H, SH), 7.05 (s, 1H, Ar-H), 6.45 (s, 2H, NH\(_2\)), 3.91 (s, 2H, CH\(_2\)), 2.31 (s, 3H, CH\(_3\)). Anal. Calcd. (%) for C\(_7\)H\(_8\)N\(_4\)O\(_4\)S\(_2\): C - 36.83, H - 3.53, N - 24.54. Found (%): C - 36.89, H - 3.58, N - 24.59.

4.2.3. Synthesis of 4-((4-((5-mercapto-1,3,4-oxadiazol-2-yl)methyl)-5-methylthiazol-2ylimino)methyl)benzene-1,2-diol (MOMMBD)

Compound 4 (2 mmol) with 3,4-dihydroxybenzaldehyde (2 mmol) in ethanol (30 mL) and 2 to 3 ml of glacial acetic acid was refluxed for 6 h. The reaction mixture was cooled by adding ice water. The formed precipitate was filtered off, washed with water and crystallized from ethanol to obtain the desired Schiff base. Yield: 71 %, M. R (°C): 141-143, IR (nujol, cm\(^{-1}\)): 3416 (OH), 1574 (-CH=N-), \(^1\)H NMR (CDCl\(_3\), \(\delta\) ppm): 13.05 (s, 1H, SH), 10.02 (s, 2H, 2OH), 8.62 (s, 1H, -CH=N-), 7.35-6.85 (m, 3H, Ar-H), 3.61 (s, 2H, CH\(_2\)), 2.32 (s, 3H, CH\(_3\)). MS, m/z: 349 (M+1). Anal. Calcd. (%) for C\(_{14}\)H\(_{12}\)N\(_4\)O\(_3\)S\(_2\): C - 48.26, H - 3.47, N - 16.08. Found (%): C - 48.32, H - 3.52, N - 16.11. the \(^1\)H NMR and mass spectra of MOMMBD is showed in Figs. 4.2. and 4.3.

4.2.4. Synthesis of 4-((4-((5-mercapto-1,3,4-oxadiazol-2-yl)methyl)-5-methylthiazol-2ylimino)methyl)-2,6-dimethoxyphenol (MOMMDP)

Compound 4 (2 mmol) with 4-hydroxy-3,5-dimethoxybenzaldehyde (2 mmol) in ethanol (30 mL) and 2 to 3 ml of glacial acetic acid was refluxed for 6 h. The reaction mixture was cooled by adding ice water, the formed precipitate was filtered off, washed with water and crystallized from ethanol to obtain the desired Schiff base. Yield: 79 %, M. R (°C): 200-202, IR (nujol, cm\(^{-1}\)): 3426 (OH), 1603 (-CH=N-). \(^1\)H NMR (CDCl\(_3\), \(\delta\) ppm):
13.05 (s, 1H, SH), 9.13 (s, 1H, OH), 8.62 (s, 1H, -CH=N-), 7.08 (s, 2H, Ar-H), 3.83 (s, 6H, 2 OCH₃), 3.61 (s, 2H, CH₂), 2.30 (s, 3H, CH₃). MS, m/z: 393 (M+1). Anal. Calcd. (%) For C₁₆H₁₆N₄O₄S₂ (%): C - 48.97, H - 4.11, N - 14.28. Found (%): C - 48.93, H - 4.08, N - 14.31. ¹H NMR and mass spectra of MOMMDP is displayed in Figs. 4.4. and 4.5.

Fig. 4.1: Scheme for the synthesis of oxadiazoles.
Fig. 4.2: $^1$H NMR spectrum of 4-((5-mercapto-1,3,4-oxadiazol-2-ylimino)methyl)-5-methylthiazol-2-ylimino) methyl) benzene-1,2-diol (MOMMBD).
Fig. 4.3: Mass spectrum of \(4-\{4-\{5\text{-mercapto-1,3,4-oxadiazol-2-yl}\text{imino}\}\text{methyl}\text{-}5\text{-methylthiazol-2-yl}\text{imino}\}\text{methyl}\) benzene-1,2-diol (MOMMBD).
Fig. 4.4: $^1$H NMR spectrum of 4-((4-((5-mercapto-1,3,4-oxadiazol-2-yl) methyl) -5-methylthiazol-2-ylimino) methyl)-2,6-dimethoxyphenol (MOMMDP).
Fig. 4.5: Mass spectrum of 4-((4-((5-mercapto-1,3,4-oxadiazol-2yl) methyl) -5-methylthiazol-2-ylimino) methyl)-2,6-dimethoxyphenol (MOMMDP).
4.3. Results and discussion

4.3.1. Antioxidant activity

The *in vitro* antioxidant activity of compounds MOMMBD and MOMMDP were determined spectrophotometrically by DPPH method and the results are given in Table 4.1. DPPH radicals are stable free radicals, and in the presence of molecules capable of donating H atoms, its radical character is neutralized [23]. The reduction capacity of DPPH radicals was determined by the decrease in its absorbance at 517 nm, which is induced by antioxidants. On the other hand, it is well-established that organic molecules incorporating an electron donating groups (amine, hydroxyl and methoxy) can act as free radical trapping agents and are capable of opposing oxidative challenges. It can be seen from Table 4.1 that compounds MOMMBD and MOMMDP present the good scavenging activity on DPPH•. The compounds bearing a hydroxyl group (electron donating group) at para position showed dominate DPPH activity with an IC$_{50}$ value of 13.5 and 14.0 µg/mL, respectively.

The synthesized compounds were also screened for hydroxyl radical and nitric oxide scavenging assays. Hydroxyl radical (•OH) scavenging capacity of the compounds is directly related to its antioxidant activity as depicted in Table 4.1. Compounds MOMMBD and MOMMDP are found to show better inhibition with IC$_{50}$ 14.8 and 17.01 µg/mL, respectively, compared with standard BHA (15.3 µg/mL). Compounds MOMMBD and MOMMDP inhibit nitric oxide with IC$_{50}$ values of 14.3µg/ml and 16.0µg/ml. The IC$_{50}$ value of MOMMBD is less than that of the standard (14.8µg/ml), whereas IC$_{50}$ value of MOMMDP is greater than that of the standard.

Table 4.1: IC$_{50}$ values for evaluated antioxidant assays of MOMMBD and MOMMDP

<table>
<thead>
<tr>
<th>Compounds</th>
<th>DPPH (µg/mL)</th>
<th>HO$^\cdot$ (µg/mL)</th>
<th>NO$^\cdot$ (µg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOMMBD</td>
<td>13.5±0.43</td>
<td>14.8±0.15</td>
<td>14.3±0.19</td>
</tr>
<tr>
<td>MOMMDP</td>
<td>14.0±0.17</td>
<td>17.1±0.01</td>
<td>16.0±0.38</td>
</tr>
<tr>
<td>AA$^a$</td>
<td>12.6±0.43</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BHA$^b$</td>
<td>-</td>
<td>15.3±0.76</td>
<td>14.6±0.11</td>
</tr>
</tbody>
</table>

$^a$ ascorbic acid

$^b$ butylated hydroxyanisole
4.3.2. Antioxidant activity and corrosion inhibition

Antioxidants from natural sources have high bioavailability, therefore high protective efficiency against free radicals [24]. Free radicals and singlet oxygen scavengers (antioxidants) were found to have metal and alloy corrosion inhibition character, which depend to a greater extent on the structural feature of the antioxidant added and to its accepting - donating hydrogen or electron behaviors [25]. In this connection, and on the basis of available results obtained by antioxidant activity measurements, we undertook the examination of corrosion inhibition studies of compounds MOMMBD and MOMMDP. The results showed that compounds MOMMBD and MOMMDP are good corrosion inhibitors with maximum inhibition efficiencies $IE$ (%) values of 87.88 and 80.00, respectively. Greater antioxidant activity and corrosion inhibition behaviour of compound MOMMBD is linked to the electron donating effect of the two hydroxyl groups attached to aromatic ring, which increases the electron density on the benzene ring. The increasing delocalization of electron density in the molecules make more reactive towards scavenging reactive oxygen as well as inhibiting corrosion process. The adsorption of inhibitor molecules is further stabilized by participation of $\pi$-electrons of benzene ring. Electronegative oxygen, sulfur and nitrogen atoms present in compounds MOMMBD and MOMMDP facilitate more efficient adsorption of the molecules on MS surface. Reduction of oxygen availability in the corroding system and the presence of a barrier between the electrode surface and oxygen retarding the rate of metal corrosion [26].

4.3.3. Mass loss measurements

The values of $IE$ (%) and corrosion rate obtained from weight loss method at different concentrations of the inhibitors at different temperatures are summarized in Table 4.2. It has been found that, compounds MOMMBD and MOMMDP inhibit the corrosion of MS at all studied concentrations. The corrosion rate decreased as the concentration of MOMMBD and MOMMDP increases up to $14.37 \times 10^{-4}$ M and $12.76 \times 10^{-4}$ M, respectively. This could be attributed to the increase in adsorption of the inhibitors onto the MS surface [27].

The variation of $IE$ (%) with temperature and inhibitor concentration is shown in Figs. 4.4 and 4.5. It can be seen that $IE$ (%) at different concentrations of MOMMBD and MOMMDP causes a significant decrease with increase in temperature from 303 - 333 K.
This behavior could be attributed to decrease in the strength of the adsorption process at higher temperatures. The lone pair of electron on the nitrogen atom will co-ordinate with the metal atoms of actives sites. Also, the presence of higher electron density in the inhibitor molecules causes stronger interaction with metal surface. The nitrogen atoms can donate π electrons to the metal surface to increase adsorption and hence inhibit the corrosion process [28]. The presence of electron donating OH groups in MOMMBD and OCH₃ group in MOMMDP increases the electron density of the benzene ring. However, the OCH₃ group in MOMMDP increases moderately the localization of lone pair of electrons on nitrogen atoms.
Table 4.2: $C_R$ and $IE$ (%) obtained from weight loss measurements of MS in 0.5 M HCl containing various concentrations of MOMMBD and MOMMDP at different temperatures

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$C \times 10^4$ (M)</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_R$ (mg cm$^{-2}$ h$^{-1}$)</td>
<td>$IE$ (%)</td>
<td>$C_R$ (mg cm$^{-2}$ h$^{-1}$)</td>
<td>$IE$ (%)</td>
<td>$C_R$ (mg cm$^{-2}$ h$^{-1}$)</td>
</tr>
<tr>
<td>MOMMBD</td>
<td>0</td>
<td>0.4276</td>
<td>-</td>
<td>0.5781</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.75</td>
<td>0.1024</td>
<td>76.05</td>
<td>0.1584</td>
<td>72.60</td>
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<td>75.57</td>
</tr>
<tr>
<td></td>
<td>11.49</td>
<td>0.0724</td>
<td>83.07</td>
<td>0.1162</td>
<td>79.90</td>
</tr>
<tr>
<td></td>
<td>14.37</td>
<td>0.0518</td>
<td>87.88</td>
<td>0.0962</td>
<td>83.36</td>
</tr>
<tr>
<td>MOMMDP</td>
<td>5.10</td>
<td>0.1345</td>
<td>68.54</td>
<td>0.1992</td>
<td>65.54</td>
</tr>
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<td></td>
<td>7.65</td>
<td>0.1164</td>
<td>72.78</td>
<td>0.1822</td>
<td>68.48</td>
</tr>
<tr>
<td></td>
<td>10.20</td>
<td>0.1024</td>
<td>76.05</td>
<td>0.1542</td>
<td>73.32</td>
</tr>
<tr>
<td></td>
<td>12.76</td>
<td>0.0855</td>
<td>80.00</td>
<td>0.1322</td>
<td>77.13</td>
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</table>
Fig. 4.6: Variation of inhibition efficiency with temperature and inhibitor concentration in the absence and presence of different concentrations of MOMMBD.

Fig. 4.7: Variation of inhibition efficiency with temperature and inhibitor concentration in the absence and presence of different concentrations of MOMMDP.
4.3.4. Effect of temperature

The activation parameters play important role in understanding the inhibitive mechanism of MOMMBD and MOMMDP. Results of $IE (%)$ obtained at different temperatures reveal that, increasing temperature increases the corrosion rate and decreases $IE (%)$. The dependence of corrosion rate on temperature can be expressed by the following Arrhenius equation:

$$C_R = A \exp \left( \frac{-E_a}{RT} \right)$$  \hspace{1cm} (4.1)

where $E_a$ is the apparent activation energy, $T$ is the absolute temperature, $A$ is the Arrhenius pre-exponential constant and $R$ is the universal gas constant. The apparent activation energy and pre-exponential factor for different concentrations of the inhibitor were calculated from the plots of logarithm of $C_R$ versus $1/T$ (Figs. 4.8 and 4.9) and the results are shown in Table 4.3. It was found that higher values of $E_a$ in the presence of inhibitors indicate more energy is required for dissolution of the MS in 0.5 M HCl [29]. This means that, the presence of inhibitor induces an energy barrier for the corrosion reaction and this barrier increases with increase in inhibitor concentration. Enthalpy and entropy of activation were calculated using the alternative form of Arrhenius equation (4.2).

$$C_R = \frac{RT}{Nh} \exp \frac{\Delta S}{R} \exp \left( -\frac{\Delta H}{RT} \right)$$  \hspace{1cm} (4.2)

where $h$ is Planck’s constant and $N$ is Avogadro’s number, $R$ is the universal gas constant, $\Delta H$ is the enthalpy of activation and $\Delta S$ is the entropy of activation. Using Eq. (4.2), plots of log ($C_R/T$) versus $1/T$ gave straight lines (Figs. 4.10 and 4.11) with a slope of $(-\Delta H /2.303R)$ and an intercept of $[\log (R/Nh) + \Delta S /2.303R]$. From the plot, the values of $\Delta H$ and $\Delta S$ are calculated and tabulated in Table 4.3. The positive values of $\Delta H$ both in the absence and presence of MOMMBD and MOMMDP reflect the endothermic nature of the MS dissolution and it indicates that the dissolution of MS is difficult. Further, the values $\Delta H$ obtained from the Eq. (4.2) and those values obtained from equation, $\Delta H = E_a - RT$ are in good agreement with each other. The entropy of activation values are less negative for inhibited solutions than that for the uninhibited solutions. This suggests that an increase in randomness occurred while moving from reactants to the activated complex [28]. Large and negative values of $\Delta S$ in uninhibited and inhibited solutions implies that the activated
complex in the rate determining step represents an association rather than dissociation step, means, decrease in disordering takes place on going from reactants to the activated complex [30, 31].

Fig. 4.8: Arrhenius plots for MS in 0.5 M HCl in the absence and presence of different concentrations of MOMMBD.
Chapter - IV

Synthesis and Anticorrosive Activity of Oxadiazoles

Fig. 4.9: Arrhenius plots for MS in 0.5 M HCl in the absence and presence of different concentrations of compound MOMMDP.

![Arrhenius plots for MS in 0.5 M HCl in the absence and presence of different concentrations of compound MOMMDP.](image)

Fig. 4.10: Alternative Arrhenius plots for MS in 0.5 M HCl in the absence and presence of different concentrations of MOMMBD.

![Alternative Arrhenius plots for MS in 0.5 M HCl in the absence and presence of different concentrations of MOMMBD.](image)

Fig. 4.11: Alternative Arrhenius plots for MS in 0.5 M HCl in the absence and presence of different concentrations of MOMMDP.

![Alternative Arrhenius plots for MS in 0.5 M HCl in the absence and presence of different concentrations of MOMMDP.](image)
**Table 4.3:** Activation parameters for MS in 0.5 M HCl in the absence and presence of different concentrations of MOMMBD and MOMMDP

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>C×10^4 (M)</th>
<th>E_a (kJ mol⁻¹)</th>
<th>k (mg cm⁻² h⁻¹)</th>
<th>ΔH (kJ mol⁻¹)</th>
<th>ΔH=E_a - RT (kJ mol⁻¹)</th>
<th>ΔS (J mol⁻¹ K⁻¹)</th>
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<tbody>
<tr>
<td>0</td>
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<td>25585</td>
<td>25.17</td>
<td>25.30</td>
<td>-169.39</td>
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<td>39.25</td>
<td>568852</td>
<td>36.62</td>
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<td>-143.59</td>
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</tr>
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<td>1261828</td>
<td>39.11</td>
<td>39.24</td>
<td>-136.90</td>
</tr>
</tbody>
</table>

**4.3.5. Adsorption considerations**

In order to get a better understanding of the adsorption mode of the inhibitor on the metal surface, the data were tested graphically by fitting to various isotherms to find the best isotherm which describes this study. Langmuir adsorption isotherm was found to fit well with the experimental data (Figs. 4.12 and 4.13). The strong correlation (R² > 0.99) suggests that the adsorption of inhibitors on the MS surface obeyed this isotherm. According to this isotherm, θ is related to the C and equilibrium constant of adsorption K_ads, using equation (4.5).

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

(4.5)

The standard Gibbs free energy of adsorption (ΔG_{ads}) can be obtained using the following equation (4.6).

\[
K_{ads} = \frac{1}{55.5} \exp \left( \frac{-\Delta G_{ads}}{RT} \right)
\]  

(4.6)

where R is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution (mol L⁻¹). This isotherm is based on the assumption that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. Using equation (4.6), the calculated ΔG_{ads} values are tabulated in Table 4.4. In general, the values of ΔG_{ads} around - 20 kJ mol⁻¹ or less negative are associated
with an electrostatic interaction between charged inhibitor molecules and charged electrode surface, i.e., physisorption and those of - 40 kJ mol\(^{-1}\) or more negative involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type bond, i.e., chemisorption [32]. The calculated values of \(\Delta G_{\text{ads}}\) for the studied inhibitors MOMMBD and MOMMDP are ranging from - 34.30 to - 37.07 and - 33.96 to - 36.38 kJ mol\(^{-1}\), respectively as presented in Table 4.4 indicating adsorption of these inhibitors involves combination of both physisorption and chemisorption, and similar observation was reported by Naik et al [33]. The higher values of \(K_{\text{ads}}\) refer to higher adsorption and higher inhibiting effect of inhibitors [34].

The calculated values of \(\Delta G_{\text{ads}}\) for the studied inhibitors MOMMBD and MOMMDP are ranging from - 34.30 to - 37.07 and - 33.96 to - 36.38 kJ mol\(^{-1}\), respectively as presented in Table 4.4 indicating adsorption of these inhibitors involves combination of both physisorption and chemisorption, and similar observation was reported by Naik et al [33]. The higher values of \(K_{\text{ads}}\) refer to higher adsorption and higher inhibiting effect of inhibitors [34]. The enthalpy and entropy of adsorption (\(\Delta H_{\text{ads}}\) and \(\Delta S_{\text{ads}}\)) can be calculated using the following equation:

\[
\ln K_{\text{ads}} = \ln \frac{1}{55.5} - \frac{\Delta H_{\text{ads}}}{RT} + \frac{\Delta S_{\text{ads}}}{R} \quad (4.7)
\]

Using Eq. (4.7), the values of \(\Delta H_{\text{ads}}\) and \(\Delta S_{\text{ads}}\) were evaluated from the slope and intercept of the plot of \(\ln K_{\text{ads}}\) versus \(1/T\) (Fig. 4.14). The negative values of \(\Delta H_{\text{ads}}\) (Table 4.4) reflect the exothermic behavior of the adsorption of inhibitors on the MS surface. The values of \(\Delta S_{\text{ads}}\) are positive in the adsorption process indicating increase in solvent entropy [35]. The reason is that the adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compound in the aqueous phase \([\text{Org}_{(\text{sol})}]\) and water molecules at the electrode surface \([\text{H}_2\text{O}_{(\text{ads})}\]) [36-38]. In this situation, the adsorption of MOMMBD and MOMMDP are accompanied by desorption of water molecules from the electrode surface. The positive values of \(\Delta S_{\text{ads}}\) suggest that gain in entropy is the driving force for the adsorption of inhibitors on the MS surface [39].

The values of \(\Delta H_{\text{ads}}\) and \(\Delta S_{\text{ads}}\) can also be calculated by using following equation:

\[
\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T \Delta S_{\text{ads}} \quad (4.8)
\]

Using Eq. (4.8), the plot of \(\Delta G_{\text{ads}}\) versus \(T\) gave a straight line (Fig. 4.15) with a slope of \(-\Delta S_{\text{ads}}\) and intercept of \(\Delta H_{\text{ads}}\). The values obtained were well correlated with those obtained from Eq. (4.7), confirming the exothermic behavior of the adsorption of the studied inhibitors on MS in 0.5 M HCl.
**Table 4.4:** Thermodynamic adsorption parameters for adsorption of MOMMBD and MOMMDP on MS in 0.5 M HCl at different temperatures from Langmuir adsorption isotherm

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Temperature (K)</th>
<th>$R^2$</th>
<th>$K_{ads}$ (L mol$^{-1}$)</th>
<th>$\Delta G_{ads}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_{ads}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_{ads}$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOMMBD</td>
<td>303</td>
<td>0.996</td>
<td>15873</td>
<td>-34.49</td>
<td>-8.43(a)</td>
<td>86.16(a)</td>
<td>-34.30</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.997</td>
<td>15151</td>
<td>-35.50</td>
<td>-8.55(b)</td>
<td>86.00(b)</td>
<td>-35.50</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.995</td>
<td>13513</td>
<td>-36.33</td>
<td>-8.55(b)</td>
<td>86.00(b)</td>
<td>-36.33</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>0.990</td>
<td>11764</td>
<td>-37.07</td>
<td></td>
<td></td>
<td>-37.07</td>
</tr>
<tr>
<td>MOMMDP</td>
<td>303</td>
<td>0.998</td>
<td>13513</td>
<td>-34.08</td>
<td>-10.29(a)</td>
<td>78.47(a)</td>
<td>-33.96</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>0.996</td>
<td>11627</td>
<td>-34.81</td>
<td>-10.33(b)</td>
<td>78.00(b)</td>
<td>-34.74</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.991</td>
<td>10869</td>
<td>-35.74</td>
<td></td>
<td></td>
<td>-35.74</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>0.993</td>
<td>9174.3</td>
<td>-36.38</td>
<td></td>
<td></td>
<td>-36.38</td>
</tr>
</tbody>
</table>

(a) Values obtained from Eq. (4.7)
(b) Values obtained from Eq. (4.8)
Fig. 4.12: Langmuir adsorption isotherm on MS in 0.5 M HCl at different temperatures of compound MOMMBD.

Fig. 4.13: Langmuir adsorption isotherm on MS in 0.5 M HCl at different temperatures of compound MOMMDP.
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Fig. 4.14: Plot of $\ln K_{\text{ads}}$ versus $1/T$.

Fig. 4.15: Plot of $\Delta G_{\text{ads}}$ versus absolute temperature.
4.3.6. Electrochemical Impedance Spectroscopy (EIS)

The corrosion of MS in 0.5 M HCl solution in the presence of MOMMBD and MOMMDP was investigated by EIS method. Nyquist plots in the absence and presence of the inhibitors are presented in Figs. 4.16 and 4.17. It is apparent that all Nyquist plots show a single capacitive loop, both in uninhibited and inhibited solutions. The impedance data of MS in 0.5 M HCl are analyzed using the equivalent circuit discussed in chapter two, section 2.2.6, which includes the solution resistance \( (R_s) \), polarization resistance \( (R_P) \) and double layer capacitance \( (C_{dl}) \). The experimental results of EIS measurements for the corrosion of MS in 0.5 M HCl medium in the absence and presence of MOMMBD and MOMMDP are given in Table 4.5. Inspection of the Table 4.5 shows that \( R_P \) values increased with the increasing concentrations of inhibitors. On the other hand, the values of \( C_{dl} \) decreased with increase in the inhibitors concentration. This situation was the result of an increase in the surface coverage by the inhibitor, which led to an increase in the \( IE \) (%). The decrease in the \( C_{dl} \), which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggest that the compounds MOMMBD and MOMMDP function by adsorption at the metal/solution interface [40]. The \( R_P \) values increases as the inhibitor concentration is raised. This indicates that the resistance towards charge transfer reaction responsible for corrosion process. These observations clearly prove the dependence of inhibitors concentration on corrosion control. The \( IE \) (%) obtained from weight loss and electrochemical measurements are in good agreement with each other at all concentrations. It is seen that addition of inhibitor increases the value of \( R_P \) from 208.9 to 454.5 \( \Omega \) cm\(^2\) for MOMMBD and 157.5 to 278.3 \( \Omega \) cm\(^2\) for MOMMDP.
Fig. 4.16: Nyquist plots for MS in 0.5 M HCl containing different concentrations of MOMMBD.

Fig. 4.17: Nyquist plots for MS in 0.5 M HCl containing different concentrations of MOMMDP.
4.3.7. Potentiodynamic polarization measurements

The results of cathodic and anodic polarization measurements on MS in 0.5 M HCl solutions containing different concentrations of MOMMBD and MOMMDP are shown in Figs. 4.18 and 4.19 as Tafel plots. Inspection of the figures clearly indicate that the inhibitors shifted both anodic and cathodic branches of Tafel curves to lower values of current density, indicating that MOMMBD and MOMMDP act as mixed type of corrosion inhibitors. This means that, the addition of inhibitor molecules to HCl solution reduces the anodic dissolution of MS and also retards the cathodic hydrogen evolution reaction [41]. Increase in the concentration of MOMMBD and MOMMDP leads to shifting the corrosion potential to a more positive value relative to the blank. Both anodic and cathodic current densities obtained in 0.5 M HCl solutions in the presence of inhibitors are lower than corrosion current densities obtained in the absence of inhibitors. The electrochemical polarization parameters such as current density ($i_{corr}$), anodic ($\beta_a$) and cathodic ($\beta_c$) slopes and the corresponding $IE$ (%) values at different concentrations of MOMMBD and MOMMDP were obtained by Tafel extrapolation at the corrosion potential ($E_{corr}$) and are reported in Table 4.5.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>C ×10^4 (M)</th>
<th>$R_p$ (Ω cm²)</th>
<th>$C_{dl}$ (µF cm⁻²)</th>
<th>$IE$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50.02</td>
<td>76.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOMMBD</td>
<td>5.75</td>
<td>208.9</td>
<td>54.15</td>
<td>76.05</td>
</tr>
<tr>
<td></td>
<td>8.62</td>
<td>253.6</td>
<td>47.39</td>
<td>80.27</td>
</tr>
<tr>
<td></td>
<td>11.49</td>
<td>303.2</td>
<td>40.93</td>
<td>83.50</td>
</tr>
<tr>
<td></td>
<td>14.37</td>
<td>454.5</td>
<td>35.20</td>
<td>88.90</td>
</tr>
<tr>
<td>MOMMDP</td>
<td>5.10</td>
<td>157.5</td>
<td>55.18</td>
<td>68.24</td>
</tr>
<tr>
<td></td>
<td>7.65</td>
<td>183.1</td>
<td>52.37</td>
<td>72.68</td>
</tr>
<tr>
<td></td>
<td>10.20</td>
<td>237.8</td>
<td>48.28</td>
<td>78.96</td>
</tr>
<tr>
<td></td>
<td>12.76</td>
<td>278.3</td>
<td>38.06</td>
<td>82.02</td>
</tr>
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</table>

Table 4.5: Electrochemical impedance parameters for MS in 0.5 M HCl in the absence and presence of different concentrations of MOMMBD and MOMMDP
Inspection of Table 4.5 clearly revealed that, the increase in inhibition efficiency \( IE(\%) \) is associated with the shift of both cathodic and anodic branches of the polarization curves towards lower current densities. Due to the presence of some active sites such as aromatic rings, hetero-atoms, the inhibitors act as adsorption inhibitors. Being absorbed on the metal surface, these compounds controlled the anodic and cathodic reactions during corrosion process, and their corrosion inhibition efficiencies are directly proportional to the amount inhibitors concentration. The \( IE(\%) \) values determined using polarization measurements are in good agreement with those obtained by EIS measurements.

**Fig. 4.18:** Potentiodynamic polarization curves for MS in 0.5 M HCl containing different concentrations of MOMMBD.

**Fig. 4.19:** Potentiodynamic polarization curves for MS in 0.5 M HCl containing different concentrations of MOMMDP.
Table 4.6: Electrochemical polarization parameters for MS in 0.5 M HCl in the absence and presence of different concentrations of MOMMBD and MOMMDP

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>C x 10^4 (M)</th>
<th>E_{corr} (mV)</th>
<th>I_{corr} (µA cm(^{-2}))</th>
<th>$\beta_a$ (mA dec(^{-1}))</th>
<th>$\beta_c$ (mA dec(^{-1}))</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.508</td>
<td>261.7</td>
<td>11.28</td>
<td>8.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOMMBD</td>
<td>5.75</td>
<td>-0.474</td>
<td>64.36</td>
<td>14.93</td>
<td>7.93</td>
<td>75.40</td>
</tr>
<tr>
<td></td>
<td>8.62</td>
<td>-0.470</td>
<td>48.90</td>
<td>17.99</td>
<td>6.37</td>
<td>81.31</td>
</tr>
<tr>
<td></td>
<td>11.49</td>
<td>-0.471</td>
<td>39.62</td>
<td>14.26</td>
<td>5.70</td>
<td>84.86</td>
</tr>
<tr>
<td></td>
<td>14.37</td>
<td>-0.478</td>
<td>30.70</td>
<td>19.77</td>
<td>7.47</td>
<td>88.26</td>
</tr>
<tr>
<td>MOMMDP</td>
<td>5.10</td>
<td>-0.473</td>
<td>82.81</td>
<td>13.91</td>
<td>7.02</td>
<td>68.35</td>
</tr>
<tr>
<td></td>
<td>7.65</td>
<td>-0.483</td>
<td>67.98</td>
<td>13.75</td>
<td>6.58</td>
<td>74.02</td>
</tr>
<tr>
<td></td>
<td>10.20</td>
<td>-0.482</td>
<td>52.69</td>
<td>16.81</td>
<td>7.51</td>
<td>79.86</td>
</tr>
<tr>
<td></td>
<td>12.76</td>
<td>-0.481</td>
<td>43.20</td>
<td>20.12</td>
<td>6.96</td>
<td>83.49</td>
</tr>
</tbody>
</table>

4.3.8. Surface analysis

The formation of a protective film of inhibitors on the MS surface was further confirmed by SEM observations. Fig. 4.20(a) shows SEM image of the polished MS surface. Fig. 4.20(b) shows surface of the MS specimen after immersion in 0.5 M HCl solution for 4 hr, while Figs 4.20(c) and 4.20(d) show MS specimens after immersion in 14.95x10^-4 M and 13.21x10^-4 M of MOMMBD and MOMMDP, respectively. After exposure of MS surface to uninhibited solution, the increase in the number of pits is observed on the surface [Fig 4.20(b)]. Fig. 4.20(c) and 4.20(d) show the protected MS surface after the addition of inhibitors MOMMBD and MOMMDP to acid solutions. MOMMBD and MOMMDP have strong tendency to adhere to the MS surface.
Fig. 4.20: SEM images of MS in 0.5 M HCl after 4 h immersion (a) before immersion (polished) (b) without inhibitor (blank) (c) with 14.37×10⁻⁴ M MOMMBD (d) with 12.76×10⁻⁴ M MOMMDP.

4.3.9. FTIR studies

FTIR is a powerful technique used to determine the type of bonding between the organic inhibitors and the metal ion. FTIR spectral analysis of the inhibitor film removed mechanically from the MS surface was carried out. Comparison of FTIR spectra of pure MOMMBD and MOMMDP with those of inhibitors film removed mechanically from the MS surface was performed and given in Figs. 4.21(a), 4.21(b), 4.21(c) and 4.21(d). It is seen from the FTIR spectra of inhibitor film mechanically removed from the MS surface that the intensity of the peaks are decreased and stretching frequencies are also decreased which implies that these compounds are coordinated to Fe⁺² resulting in the formation of Fe⁺²-inhibitor complex on the metal surface.

Fig. 4.21(a) illustrates the FTIR spectrum of the MOMMBD. The strong broad band at 2548 and 3541 cm⁻¹ are attributed to S-H and O-H stretching. The absorption bands at 2924 cm⁻¹ is related to -CH₂ asymmetrical stretching vibration. The bands at 1545 and 1458 cm⁻¹ are assigned to C=C stretching vibrations. The band around 1044 cm⁻¹ is the stretching vibration of C-O in oxadiazole ring. The band at 1662 cm⁻¹ indicates the stretching vibration of C=N. Hence, it can be inferred that MOMMBD contains oxygen and nitrogen atoms in the functional groups (O-H, S-H, C=N, C–O, C=C) and aromatic ring which meets the general structural consideration of the corrosion inhibitors.
Fig. 4.21(b) illustrates the FTIR spectrum of the surface film scrapped from the MS specimen after 4 h immersion in 0.5 M HCl containing MOMMBD. Comparison with the FTIR spectrum of the pure MOMMBD [Fig. 4.21(a)] indicates that the band corresponds to S-H at 2548 cm\(^{-1}\) was found to be disappeared and O-H stretching frequency at 3541 cm\(^{-1}\) is slightly shifted to 3446 cm\(^{-1}\). The \(-\text{CH}_2\) asymmetrical stretching vibration was decreased from 2924 to 2881 cm\(^{-1}\). The band at 1662 cm\(^{-1}\) corresponds to C=N stretching vibration is shifted to 1632 cm\(^{-1}\). These observations clearly indicate the formation of the metal – inhibitor complex which is responsible for preventing corrosion.

Fig. 4.21(c) illustrates the FTIR spectrum of the pure MOMMDP. The strong broad bands at 2677 cm\(^{-1}\) and 3607 cm\(^{-1}\) are attributed to S-H and O-H stretching. The band at 1456 cm\(^{-1}\) is assigned to C=C stretching vibrations. A band around 1044 cm\(^{-1}\) is the stretching vibration of C-O in oxadiazole ring. The band at 1658 cm\(^{-1}\) indicates the stretching vibration of C=N. Hence, it can be inferred that compound MOMMDP contains oxygen and nitrogen atoms in functional groups (O-H, S-H, C=N, C-O, C=C) and aromatic ring, which meets the general structural consideration of the corrosion inhibitors.

Fig. 4.21(d) illustrates the FTIR spectrum of the surface film on the MS specimen after 4 h immersion in 0.5 M HCl containing MOMMDP. Comparison with the FTIR spectrum of the pure MOMMDP [Fig 4.19(c)] indicates that the band corresponds to S-H at 2677 cm\(^{-1}\) is found to be disappearing and O-H stretching frequency at 3607 cm\(^{-1}\) is slightly shifted to 3586 cm\(^{-1}\). The band at 1658 cm\(^{-1}\) corresponds to C=N stretching vibration is shifted to 1628 cm\(^{-1}\). These observations clearly indicate the formation of the metal – inhibitor complex which is responsible for preventing corrosion.
Fig. 21: FTIR spectra of (a) pure MOMMBD (b) surface film of the MS specimen after immersion in 0.5 M HCl containing MOMMBD (c) pure MOMMDP (d) surface film of the MS specimen after immersion in 0.5 M HCl containing MOMMDP.
4.4. Conclusion

The synthesized inhibitors MOMMBD and MOMMDP acted as potential corrosion inhibitors for MS in 0.5 M HCl. The percentage inhibition $IE$ (%) of the designed molecules increases by increasing concentration, but it decreases with increasing temperature. The adsorption of the inhibitors on the MS surface follows Langmuir isotherm model. The negative sign of the $\Delta H_{\text{ads}}$ indicates that the adsorption process is spontaneous and exothermic. The high $K_{\text{ads}}$ values indicate a strong interaction between inhibitors and the metal surface. The polarization curves indicate that MOMMBD and MOMMDP act as mixed type of inhibitors. AC impedance plots of MS indicate that polarization resistance increases with increase in inhibitors concentration. Morphological investigation suggests that, addition of inhibitors in the aggressive solution results in the formation of the protective film on MS surface. FTIR results indicate the presence of a uniform and dense adsorptive film over the MS surface, which efficiently inhibits the corrosion of MS. The results obtained by antioxidant activity measurements of inhibitors are correlated with their inhibition efficiency $IE$ (%).
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