Study of sulfanyl pyridazine derivatives as efficient corrosion inhibitors for carbon steel in 1.0 M HCl using analytical techniques

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Abstract

Five new sulfur containing heterocyclic derivatives of sulfanyl pyridazine type compounds (1–5) were synthesized, characterized by FT-IR and 1H NMR, and evaluated as corrosion inhibitors for carbon steel in 1.0 M HCl at various concentration and temperatures. Five different analytical techniques were used in this study, namely, gravimetric, gasometrical, atomic absorption spectroscopy, AAS, thermometric, and acidimetric techniques. The corrosion inhibition efficiency increases with increasing inhibitor concentration but decreases with temperature. The inhibition of corrosion is due to adsorption on the metal surface and formation of a barrier film that separates the metal from the corrosive medium. The inhibition is due to physicochemical adsorption of a heterocyclic compound on steel surface, and the adsorption obeys the Langmuir isotherm. Thermodynamic parameters for both activation and adsorption were computed and discussed. The reduction in reaction number (RR%) and Δt_m increased with increasing inhibitor concentrations. The pH increased and the hydrogen ion concentration in the medium decreased upon addition of inhibitors as an inhibitor molecule acts as a ligand for protons in acidic media. The ferrous ion Fe^{+2} concentrations determined by AAS decreased in the solution with increasing inhibitor concentration. The data obtained from different analytical techniques are in good agreement within (±2%).

Keywords: atomic absorption spectroscopy AAS, corrosion inhibitors, steel, gasometrical, gravimetrical, acidimetric, thermometric, sulfanyl pyridazine.

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1. Introduction

The use of acidic corrosive solutions for various purposes (like descaling, pickling etc.) is extremely vital for these purposes. These corrosive solutions may dissolve the metallic containers. Therefore, we are striving to resolve this problem [1]. Development of methods for corrosion control is a challenge to scientists working in this area. Amongst various methods developed for corrosion protection, the use of inhibitors is among the most practical methods for protection of steel against corrosion in acidic media. Corrosion inhibitors are used to control the steel dissolution and consumption; generally, inhibitors are organic compounds that contain oxygen, sulfur, and nitrogen atoms in their chemical structure [1–10]. The inhibiting effect of these compounds is generally explained by the formation of a physical and/or chemical adsorption film barrier on the metal surface [11–13]. The adsorption properties depend on the structures of the organic inhibitors such as functional groups, steric factor and aromaticity [14–20]. Surfactant type corrosion inhibitors have many advantages such as high inhibition efficiency, low price, low toxicity and easy production. The adsorption of surfactant markedly changes the corrosion resistance of a metal. For these reasons, studying the relationship between adsorption and corrosion inhibition is significantly important [20–25]. The majority of the well-known inhibitors for the corrosion of steel in acidic media are organic compounds containing nitrogen, sulfur, oxygen atoms, or N-heterocyclic compounds with polar groups. A large number of scientific studies have been devoted to the subject of corrosion inhibitors for steel in acidic media [26–32]. Sulfanyl pyridazine derivatives are promising as they contain functional groups, sulfur, nitrogen and oxygen atoms in their structure which favor the adsorption of these inhibitors on steel surface. Sulfanyl pyridazine hydrazide derivatives with higher water solubility can also be prepared easily from the corresponding sulfanyl pyridazine ester itself. The use of sulfanyl pyridazine derivatives as corrosion inhibitors for steel is not much covered in the literature. Generally, pyridazine compounds have high biological activity and find use as anticancer, anti-tuberculosis, antihypertensive, antifungal, or antimicrobial agents. Moreover, these compounds have some medical applications due to their non-toxicity so they can be used as potential non-toxic corrosion inhibitors. The aim of this study is to synthesize novel substituted sulfanyl pyridazine derivatives bearing a side chain with different terminal function groups for the purpose of enhancing their adsorption properties and corrosion inhibition efficiency. The corrosion inhibition efficiency of the five prepared compounds was estimated using five different analytical techniques, namely gravimetrical, gasometrical, atomic absorption spectroscopy, AAS, thermometric, and acidimetric techniques. The effect of concentration and temperature on the corrosion inhibition performance of the prepared heterocyclic sulfanyl pyridazine derivatives was also studied and the thermodynamic parameters for both activation and adsorption were computed and discussed. The corrosion inhibition mechanism was suggested.
2. Experimental

2.1. Materials and test solution

The chemical compounds used in this study, namely hydrazine hydrate 99%, ethyl alcohol 98%, 2,4-dihydroxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, 4-(dimethylamino)-benzaldehyde, were purchased from Aldrich Chemical Co. Ltd. (UK) England. The carbon steel materials employed in this study had the mass composition given in Table 1. The corrosive solution used in this study is 1.0 M hydrochloric acid with pH 0.0. It was prepared from analytical grade 37% HCl (Sigma Aldrich) by dilution with double-distilled water and then titrated against 1.0 N Na₂CO₃ solution.

Table 1. Gravimetric composition of the steel materials used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>C</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition, mass%</td>
<td>0.517</td>
<td>0.201</td>
<td>0.009</td>
<td>0.007</td>
<td>0.157</td>
<td>About 99%</td>
</tr>
</tbody>
</table>

2.2. Synthesis of the inhibitors

All melting points were measured using Electro-Thermal IA 9100 apparatus (Shimadzu, Japan) and were uncorrected. Infrared spectra were recorded as potassium bromide pellets on a Perkin-Elmer 1650 spectrophotometer (Perkin-Elmer, Norwalk, CT, USA). ¹H NMR and ¹³C NMR spectra were determined on a Jeol-Ex-400 NMR spectrometer (JEOL, Tokyo, Japan) and chemical shifts were expressed as part per million (° values, ppm) against TMS as internal reference. Mass spectra were recorded on a VG 2AM-3F mass spectrometer (Thermo Electron Corporation, USA). Microanalyses were performed using Mario El Mentor apparatus, Organic Microanalysis Unit, and the results were within the accepted range (±0.20) of the calculated values.

Synthesis of (6-phenyl-pyridazin-3-ylsulfanyl)-acetic acid hydrazide (2)

To a solution of compound 1 (2.74 g, 10 mmol) in ethanol (150 mL), hydrazine hydrate (6 mL, 99%) was added and the reaction mixture was heated on a water bath for 5 h. After cooling, the precipitated material was filtered off, washed with water, dried, and recrystallized from ethanol to give compound 2. Yield 85%, m.p. 256–257°C. IR (KBr) ν cm⁻¹: 3421–3244 (NH₂, NH) and 1665 (C=O) cm⁻¹. ¹H NMR (DMSO-d₆) δ ppm: 4.00 (s, 2H, CH₂), 4.31 (s, 2H, NH₂, D₂O exchangeable), 7.51–7.57 (m, 3H, Ph–H), 7.81 (d, 1H, C₄–H), 8.09–8.11 (m, 3H, 2Ph–H + C₅–H) and 9.39 (s, 1H, NH, D₂O exchangeable). ¹³C NMR (DMSO-d₆) 33.70 (CH₂S), 125.51–130.63 (C–Ph), 134.20 (C–5), 141.85 (C–4), 149.90 (C–6), 158.22 (C–3) and 169.18 (C=O). MS m/z (%): 260.32 [M⁺] (77.90). Anal. calcd. for C₁₂H₁₂N₄OS: C, 55.37; H, 4.65; N, 21.52; S, 12.32. Found: C, 55.40; H, 4.69; N, 21.49; S, 12.25.
General procedure for the synthesis of compounds (3–5)

A mixture of compound 2 (2.60 g, 10 mmol) and 2,4-dihydroxybenzaldehyde, 2-hydroxy-naphthalene-1-carbaldehyde, 4-dimethylamino-benzaldehyde (10 mmol) in absolute ethanol (50 mL) was refluxed for 3–7 h. The reaction mixture was cooled and the solid product was filtered off, dried, and recrystallized from appropriate solvents to give compounds 3–5, respectively.

\textit{(6-Phenyl-pyridazin-3-yl)sulfanyl}-acetic acid (2,4-dihydroxy-benzylidene)-hydrazide (3).

Yield 87%; m.p. 294–296°C; IR (KBr) ν cm\(^{-1}\): 1629.56 (C=N triazole), 1675.21 (C=O), 3421.81 (NH aliphatic), 3568.18 (2OH broad band); \(^1\)H NMR (DMSO-d\(_6\)) δ ppm: 4.00 (s, 2H, CH\(_2\)), 6.33 (s, 2H, 2OH), 7.51–7.69 (m, 6H, Ph–H), 7.81 (d, 1H, C\(_4\)--H), 8.09–8.11 (m, 2H, 2Ph–H), 8.12 (d, 1H, C\(_5\)--H), 8.21 (s, H, CH aliphatic), 11.86 (s, 1H, NH, D\(_2\)O exchangeable); \(^13\)C NMR (DMSO-d\(_6\)) δ ppm: 34.10 (CH\(_2\)), 125.51–130.63 (C–Ph), 134.21 (C–5), 141.85 (C–4), 148.1 (C–aliphatic), 149.90 (C–6), 158.22 (C–3) and 170.20 (C=O). MS \(m/z\) (%): 380.42 [M\(^+\)] (88.25). Anal. calcd. for C\(_{19}\)H\(_{16}\)N\(_2\)O\(_3\): C, 59.99; H, 4.24; N, 14.73; S, 8.43. Found (%): C, 60.05; H, 4.30; N, 14.70; S, 8.37.

\textit{(6-Phenyl-pyridazin-3-yl}sulfanyl}-acetic acid (2-hydroxy-naphthalen-1-ylmethylene)-hydrazide compound (4).

Yield 85%; m.p. 319–320°C; IR (KBr) ν cm\(^{-1}\): 1687.02 (C=N triazole), 1675.66 (C=O), 3420.21 (NH aliphatic), 3568.11 (OH); \(^1\)H NMR (DMSO-d\(_6\)) δ ppm: 4.00 (s, 2H, CH\(_2\)), 4.81 (s, 1H, OH), 7.21–8.78 (m, 14H, Ar–H+CH aliphatic), 11.86 (s, 1H, NH, D\(_2\)O exchangeable); MS \(m/z\) (%): 414.48 [M\(^+\)] (92.35). Anal. calcd. for C\(_{23}\)H\(_{18}\)N\(_2\)O\(_2\): C, 66.65; H, 4.38; N, 13.52; S, 7.74. Found (%): C, 66.70; H, 4.42; N, 13.48; S, 7.68.

\textit{(6-Phenyl-pyridazin-3-yl)sulfanyl}-acetic acid (4-dimethylamino-benzylidene)-hydrazide compound (5).

Yield 83%; m.p. 304–305°C; IR (KBr) ν cm\(^{-1}\): 160.48 (C=N triazole), 1676.71 (C=O), 2902.71 (NH aliphatic); \(^1\)H NMR (DMSO-d\(_6\)) δ ppm: 2.51 (s, 2H, CH\(_3\)), 4.01 (s, 2H, CH\(_2\)), 7.42–7.44 (m, 2H, 2Ph–H), 7.51–7.69 (m, 5H, Ph–H), 7.80 (d, 1H, C\(_4\)--H), 8.09–8.11 (m, 2H, 2Ph–H), 8.11 (d, 1H, C\(_5\)--H), 8.20 (s, H, CH aliphatic), 11.85 (s, 1H, NH, D\(_2\)O exchangeable); MS \(m/z\) (%): 391.49 [M\(^+\)] (75.58). Anal. calcd. for C\(_{21}\)H\(_{21}\)N\(_3\)OS: C, 64.43; H, 5.41; N, 17.89; S, 8.19. Found (%): C, 64.37; H, 5.38; N, 17.93; S, 8.25.

2.3. Gravimetric studies (weight loss measurements)

The technique is based on determining the weight loss (WL) of a sample (coupon) with surface (S) immersed for a time (t) in the corrosive solution. The tests were performed in 100 mL glass vials in non-aerated medium, at room temperature. The immersion time was 8 h. The iron samples were cleaned with distilled water, degreased with acetone and dried before and after the immersion. The determination of the corrosion rate \(R_{corr}\) was made using
The mathematical formula (1) below. The corrosion inhibition efficiency \( I.E.\% \) was calculated using mathematical formula (2), and the surface coverage (\( \theta \)), which represents the fraction of the metal surface covered by the inhibitors molecules, was calculated according to formula (3) [18, 24, 25].

2.4. Atomic absorption spectroscopy (AAS)

The quantitative content of iron ions in the corrosive solutions in the absence and presence of the drugs used as corrosion inhibitors was determined by atomic absorption spectroscopy (AAS). The concentration of ferrous ions passed into solution was determined by atomic absorption spectroscopy using a Varian Spectra AA 220 instrument.

2.5. Gasometrical measurements (hydrogen evolution measurements)

The progress of the corrosion reaction was determined by volumetric measurements of the evolved hydrogen. The metal sample was put in a Büchner flask containing the test solution. The flask was sealed with a rubber bung, and from its hose barb protruding from its neck, rubber tubing was connected to the bottom of an inverted measuring cylinder which was fitted above a basin. The cylinder and the basin were filled with distilled water. The evolved hydrogen gradually displaced the distilled water and was collected at the top inside the cylinder, and its volume variation with time was measured directly. The experiment was performed in the absence and presence of different concentrations of the tested inhibitors [14, 24].

2.6. Thermometric measurements

The carbon steel sheet with a chemical composition as mentioned in Table 1 was press cut to \( 2\times2\times0.1 \) cm dimensions. The measurements were carried out in a Dolvacpyrex flask cover with an aluminum foil sheet. The reaction vessel contained 100 ml of the acid test solution put into the flask covered with an aluminum foil sheet, corked with a Check temp digital thermometer in place. The metal coupon was introduced into the corrosive solution and quickly covered. The variation of temperature in the system was monitored with time and the reaction number (\( RN \)) was determined.

2.7. Acidification method

Each experiment was preceded by evaluation of the pH in the prepared solution by a standard BT-500 model pH meter (Germany). The pH was checked for four concentrations, 50, 100, 150, 200, and 200 ppm, pre and post dipping in the checked solution for 7 hrs. The computed \( I.E.\% \) values are shown in the Results section [39].
3. Results and Discussion

3.1. Chemistry

Sulfanyl pyridazine derivatives used as corrosion inhibitors in this study were prepared starting from compound 1 as shown in Scheme 1. (6-Phenyl-pyridazin-3-ylsulfanyl)-acetic acid hydrazide 2 was prepared by the reaction of compound 1 with hydrazine hydrate by refluxing in ethanol. The structure of compound 2 was confirmed by elemental analysis and spectral data. The IR spectra showed absorption bands of NH₂ and C=O groups, while the ¹H NMR spectra revealed signals at δ 4.31 and 9.39 ppm due to NH₂ and NH (D₂O exchangeable) and its MS spectra gave a molecular ion peak at m/z (%) = 260.32 (77.90) (cf. Experimental). Treatment of compound 2 with 2,4-dihydroxybenzaldehyde, 2-hydroxynaphthalene-1-carbaldehyde, and 4-dimethylamino-benzaldehyde afforded the corresponding Schiff base hydrazides 3–5, respectively. The structures of compounds 3–5 was confirmed by elemental analysis and spectral data. The IR and ¹H NMR spectra of these compounds revealed the absence of the NH₂ group and the presence of signals characteristic of OH groups in compounds 3 and 4. Meanwhile, the ¹³C NMR spectrum of compound 3 showed a signal characteristic of CH aliphatic as well as substituted phenyl (cf. Experimental).
3.2. Evaluation of the prepared compounds as corrosion inhibitors

3.2.1. Gravimetric measurements

3.2.1.1. Effect of concentration on the corrosion inhibition efficiency

The corrosion rate $R_{\text{corr.}}$ values were calculated using equation (1).

$$R_{\text{corr.}} = (\Delta W/\text{St})$$

Where, $\Delta W$ is the average weight loss of steel coupons in the corrosive solution, $S$ is the total surface area of the specimen, and $t$ is the immersion time.

The percentage inhibition efficiency ($I.E.$%) and the surface coverage ($\theta$), which represents the fraction of the metal surface covered by inhibitor molecules, were calculated using the following equations [12–14]:

$$I.E.\, \% = \left( \frac{R_{\text{free}} - R_{\text{add}}}{R_{\text{free}}} \right) \cdot 100$$

$$\theta = \left( \frac{R_{\text{free}} - R_{\text{add}}}{R_{\text{free}}} \right)$$

Where, $R_{\text{free}}$ and $R_{\text{add}}$ are the weight losses of carbon steel without and with addition of inhibitors, respectively [25]. The values of percentage of inhibition efficiency and surface coverage ($\theta$) of the prepared compounds are listed in Table 2. Inspection of this table reveals that the values of inhibition efficiency increases with increasing concentration of these compounds and the inhibition efficiency decreases in the order: $C_3 > C_5 > C_4 > C_2 > C_1$. This behavior is due to functional groups and solubility in aqueous medium. Figure 1 show weight loss–time curves for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of compound 3 (C3) as an example of the tested inhibitors.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration ppm</th>
<th>$R_{\text{corr}}$ mg cm$^{-2}$·hr$^{-1}$</th>
<th>I.E. %</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C3</td>
<td>50</td>
<td>0.96</td>
<td>98.3</td>
<td>0.983</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.79</td>
<td>91.2</td>
<td>0.912</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.63</td>
<td>93.0</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.52</td>
<td>94.2</td>
<td>0.942</td>
</tr>
<tr>
<td>C5</td>
<td>50</td>
<td>1.2</td>
<td>86.6</td>
<td>0.866</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.0</td>
<td>88.8</td>
<td>0.888</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.88</td>
<td>90.2</td>
<td>0.902</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.76</td>
<td>91.5</td>
<td>0.915</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration ppm</th>
<th>$R_{corr}$ mg·cm$^{-2}$·hr$^{-1}$</th>
<th>I.E. %</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4</td>
<td>50</td>
<td>1.5</td>
<td>83.3</td>
<td>0.833</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.3</td>
<td>85.5</td>
<td>0.855</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.1</td>
<td>87.77</td>
<td>0.877</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.88</td>
<td>90.1</td>
<td>0.90</td>
</tr>
<tr>
<td>C2</td>
<td>50</td>
<td>1.6</td>
<td>82</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.4</td>
<td>84</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.2</td>
<td>86.6</td>
<td>0.866</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.1</td>
<td>87.7</td>
<td>0.877</td>
</tr>
<tr>
<td>C1</td>
<td>50</td>
<td>1.9</td>
<td>78.9</td>
<td>0.789</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.8</td>
<td>80</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>1.6</td>
<td>82</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.5</td>
<td>83.3</td>
<td>0.833</td>
</tr>
</tbody>
</table>

Figure 1. Mass loss of carbon steel as a function in time in 1.0 M HCl in the absence and in the presence of compound 3 (C3).

Similar curves were obtained for the other compounds. This figure reveals that on increasing the concentration of this compound, the weight loss of carbon steel samples decreases. This means that the presence of these compounds slows down the corrosion of carbon steel in 1.0 M HCl solution, or in other words, these compounds act as good inhibitors. The linear variation of weight loss with time in uninhibited and inhibited 1.0 M HCl indicates the absence of insoluble surface films during corrosion. In this case, the inhibitors used are first adsorbed onto the metal surface and thereafter impede corrosion.
either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes [27, 38].

3.2.1.2. Effect of temperature on the corrosion inhibition efficiency

To elucidate the mechanism of inhibition and to determine the kinetic parameters of the corrosion process, weight loss measurements were performed at 303, 313, 323, and 333 K. The effect of temperature on the corrosion inhibition efficiency of carbon steel in the presence of the inhibitor is graphically represented in Figure 2.

![Figure 2](image)

**Figure 2.** Effect of temperature on I.E.% for carbon steel in 1 M HCl in the presence of different concentrations of the compound (C3).

The inhibition efficiency decreased with an increase in temperature, leading to the conclusion that the protective film of these compounds formed on the steel surface is less stable at higher temperature; this may be due to the desorption of some adsorbed molecules from the steel surface at higher temperatures due to which a greater area of the metal is exposed to the acidic environment. The apparent activation energy \( E_a \) of metal corrosion in acid media can be calculated from the Arrhenius equation [24–26]:

\[
\ln R_{\text{corr}} = \left( \frac{E_a}{R} \right) + A
\]

(4)

Where \( E_a \) is the apparent activation energy for the corrosion of carbon steel, \( R \) is the universal gas constant, \( A \) is Arrhenius pre-exponential factor and \( T \) is the absolute temperature. Figure 3 depicts the plot of \( \log R_{\text{corr}} \) vs. \( 1/T \) and the values of \( E_a \) obtained from the slope of the plot are given in Table 3.
Table 3. Values of activation parameters of carbon steel in 1.0 M HCl in the absence and presence of different concentrations of the inhibitor (C3).

<table>
<thead>
<tr>
<th>Inhibitor concentration</th>
<th>$E_a^*$</th>
<th>$\Delta H_a^*$</th>
<th>$-\Delta S_a^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm</td>
<td>kJ·mol⁻¹</td>
<td>kJ·mol⁻¹</td>
<td>J·K⁻¹·mol⁻¹</td>
</tr>
<tr>
<td>blank</td>
<td>42.6</td>
<td>42.3</td>
<td>153.5</td>
</tr>
<tr>
<td>50 ppm</td>
<td>57.5</td>
<td>54.2</td>
<td>156</td>
</tr>
<tr>
<td>100 ppm</td>
<td>59.7</td>
<td>58.7</td>
<td>149.8</td>
</tr>
<tr>
<td>150 ppm</td>
<td>62.3</td>
<td>62.8</td>
<td>146.5</td>
</tr>
<tr>
<td>200 ppm</td>
<td>64.8</td>
<td>65.6</td>
<td>143.7</td>
</tr>
</tbody>
</table>

The higher value of activation energy ($E_a$) in the presence of inhibitor than in its absence is attributed to its physical adsorption, its chemisorption is pronounced in the opposite case [18, 26, 32].

![Figure 3. Arrhenius plot for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of the inhibitor (C3).](image)

In this study, the higher value of $E_a^*$ for carbon steel in the presence of the inhibitor than in its absence is attributed to its physical adsorption. Szauer and Brand [26, 38] explained that the increase in $E_a^*$ can be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with an increase in temperature and the corresponding increase in corrosion rates occurs due to the fact that a greater area of the metal is exposed to the acid environment.

An alternative form of Arrhenius equation is the transition state equation [18, 25, 38]

$$ R_{corr} = \frac{(RT/Nh)\exp(\Delta S_a^*/R)\exp(-\Delta H_a^*/RT)}{(1/T) \cdot 10^{-3}, K^{-1}} $$

(5)

where, $h$ is the Plank’s constant, $N$ is the Avogadro’s number, $\Delta S_a^*$ is the entropy of activation, and $\Delta H_a^*$ is the enthalpy of activation. A plot of $\log(CR/T)$ vs. $1/T$ gave a straight
line as shown in Figure 4 with a slope of \((-\Delta H^*/2.303R)\) and an intercept of \([\log(R/Nh)+(\Delta S^*/R)]\), from which the values of \(\Delta H_a\) and \(\Delta S_a\) were calculated and listed in Table 3.

![Figure 4](image)

**Figure 4.** Transition state plot for carbon steel in 1.0 M HCl solution in the absence and in the presence of different concentrations of the inhibitor (C3).

The positive values of \(\Delta H_a^*\) for corrosion of carbon steel in the presence and absence of the inhibitor reflect the endothermic nature of metal dissolution process. The increase in \(\Delta H_a^*\) with an increase in the concentration of the inhibitor for mild steel corrosion reveals that the decrease in mild steel corrosion rate is mainly controlled by kinetic parameters of activation [25, 26, 38]. 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 [14, 18].

### 3.2.2. Adsorption isotherm

The adsorption process depends mainly on the charge and nature of the metal surface, electronic characteristics of the metal surface, adsorption of solvent and other ionic species, temperature of corrosion reaction, the electrochemical potential at the solution-metal interface, and the presence of electro repelling or electro donating groups in the derivatives. To choose the suitable adsorption isotherm, the degree of surface coverage (\(\theta\)) for various concentrations of the inhibitor (\(C_i\)) was calculated. The data were tested graphically by fitting to various isotherms. We found that the best results were obtained by applying Langmuir adsorption isotherm according to the following equation [2, 13, 18]:

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

where, \(K_{ads}\) is equilibrium constant of the equilibrium adsorption process.

Figure 5 represents the relationship between \(C_i/\theta\) and \(C_i\). A straight line with a slope equal to unity and the correlation coefficient nearly equal to 1.0 were obtained. This indicates that the adsorption of the used inhibitor on the carbon steel surface followed the Langmuir
adsorption isotherm model. The Langmuir isotherm assumes that an adsorbed molecule occupies only one site and does not interact with other adsorbed species.

The standard Gibbs free energy ($\Delta G_{\text{ads}}$) values are obtained by the following Equation 7:

$$K_{\text{ads}} = 1/55.5 \exp(\Delta G_{\text{ads}}/RT)$$  (7)

Where $K_{\text{ads}}$ is the adsorption equilibrium constant, 55.5 is the content of water in the bulk of solution in mole/liter, $T$ is the absolute temperature and $R$ is the gas constant. The other thermodynamic parameters ($\Delta H_{\text{ads}}$ and $\Delta S_{\text{ads}}$) are obtained by Equation 8 and 9 respectively.

$$\log K_{\text{ads}} = -(\Delta H_{\text{ads}})/RT + \text{constant}$$  (8)

$$\Delta S_{\text{ads}} = (\Delta H_{\text{ads}} - \Delta G_{\text{ads}})/T$$  (9)

The results presented in Table 4 show that the values of $\Delta G_{\text{ads}}$ are about $-39$ kJ·mol$^{-1}$, which indicates that both physical and chemical adsorption occurs. The values of $\Delta H_{\text{ads}}$ are negative indicating that the reaction is exothermic [14, 18, 25]. $\Delta S_{\text{ads}}$ values are negative indicating that the adsorption of the inhibitor on steel is more ordered. Figure 5 show the Langmuir isotherm for the inhibitor compound 3 C3 at four different temperatures.

Table 4. The adsorption parameters of the inhibitor compound 3 on the steel surface in 1.0 M HCl.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$-\Delta G_{\text{ads}}$ kJ·mol$^{-1}$</th>
<th>$-\Delta H_{\text{ads}}$ kJ·mol$^{-1}$</th>
<th>$-\Delta S_{\text{ads}}$ J·mol$^{-1}$·K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>37.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>38.4</td>
<td>21.6</td>
<td>64.7</td>
</tr>
<tr>
<td>323</td>
<td>39.3</td>
<td></td>
<td>64.3</td>
</tr>
<tr>
<td>333</td>
<td>39.8</td>
<td></td>
<td>64.5</td>
</tr>
</tbody>
</table>

Figure 5. Langmuir adsorption isotherm for carbon steel in 1.0 M HCl inhibited by the prepared compound 3 at four different temperatures.
3.2.3. Atomic absorption spectroscopy measurements (AAS)

Atomic absorption is mainly of indirect value for rapid analysis during the production process because, due to the sequential character of the technique, it cannot be used for complete steel or slag analysis in a two to three-minute period [32]. AAS was used for corrosion rate prediction in different media (acidic, basic, and neutral) based on fundamental chemistry of the solubility of the corrosion products. The AAS method was applied to the determination of Fe\textsuperscript{+2} ions in mineral waters and natural waters [33]. Iron corrosion is a complex process that occurs when iron is exposed to oxygen and humidity and is exacerbated by the presence of chloride ions. The deterioration of iron structures or other components can be costly to society and can be evaluated by following the properties of the corroding material [34]. The iron ions released into solution due to corrosion were detected directly by atomic absorption spectroscopy and their concentration was determined using a calibration curve. The corrosion of iron samples in solution was accelerated by high salinity, lowering the pH, the presence of chloride ions, and temperature [34].

In the present study, the ferrous ion Fe\textsuperscript{+2} concentrations resulting from the corrosion of iron by corrosive 1.0 M HCl solution were determined by atomic absorption spectroscopy (AAS). The concentrations of the ions passed into solution were measured using AAS. The concentrations of ferrous ions in the corrosive solution were determined both in the absence and in the presence of the inhibitor used. The data of AAS are listed in Table 5 and Figure 6. They show that the ferrous ion Fe\textsuperscript{+2} concentration decreased with increasing inhibitor concentration. Here the ferrous ions concentration was taken as a function of corrosion rate because as the ferrous ion concentration in the solution increases, the corrosion rate increases and vice versa. The process is affected by addition of the inhibitors. The data in Table 5 agree well with the results obtained by gravimetric (weight loss) method so the gravimetric techniques are in good agreement to each other to indicate that, the addition of sulfanyl pyridazine compounds inhibits the corrosion of steel in acidic environment and decreases the iron dissolution process (ferrous ion concentration Fe\textsuperscript{+2}) in this environment. AAS data indicate that the values of inhibition efficiency increase with increasing concentration of these compounds and the order of inhibition efficiency decreases in the following order: C3 > C5 > C4 > C2 > C1, as shown in Figure 6. This behavior is due to the functional groups and solubility in the aqueous medium, and agrees well with the other used techniques.

Table 5. Effect of inhibitor concentrations on ferrous ion concentrations as result from AAS technique.

<table>
<thead>
<tr>
<th>Inhibitor concentration, ppm</th>
<th>Ferrous ion concentration [Fe\textsuperscript{+2}], ppm (AAS data)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Compound no.</td>
</tr>
<tr>
<td>Blank</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>
3.2.4. Gasometrical measurements (hydrogen evolution method)

Gasometrical techniques are based on measuring the evolved amount of hydrogen gas with time in the absence and presence of inhibitors in acidic environment. In the present work, the gasometrical technique (hydrogen evolution method) was used for evaluation of the sulfanyl pyridazine derivatives as corrosion inhibitors for carbon steel in acidified 1.0 M hydrochloric acid solution. Iron metal is an active metal of higher oxidation potential so it replaces the hydrogen of an acid easily giving a metal salt and hydrogen is evolved in the gaseous form. The volume of hydrogen evolved during the corrosion reaction of iron in acidic HCl medium in the absence and presence of different concentrations of the used inhibitor, 50, 100, 150, 200 ppm was measured with time at room temperature (30°C). The inhibition efficiency was calculated using the following equation [35].

\[
I.E.\% = \left[1 - \frac{V_{inh}}{V_{free}}\right] \times 100
\]  

where, \(V_{inh}\) is the volume of hydrogen gas evolved from an inhibited solution and \(V_{free}\) corresponds to the uninhibited solution. The volumes of evolved hydrogen and inhibition efficiencies at different concentrations of the inhibitors used are shown in Table 6. The inhibition efficiency increases with increasing the inhibitor concentration, which indicates that the inhibitor compounds used act as good inhibitors for carbon steel in 1.0 M HCl acidic environment.
Table 6. Gasometrical data for the steel corrosion in acidic HCl solution without and with different concentrations of the used inhibitor at 30°C.

<table>
<thead>
<tr>
<th>Inhibitor concentrations ppm</th>
<th>Volume of hydrogen ml/cm²</th>
<th>Corrosion inhibition efficiency I.E. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound no.</td>
<td>C5</td>
<td>C3</td>
</tr>
<tr>
<td>Blank</td>
<td></td>
<td>56</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>100</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>150</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>200</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

3.2.5. Thermometric measurements

Thermometric measurements involve measuring the temperature variation during the reaction of a test metal piece with a definite volume of a corrosive solution [36]. Reaction number (RN) values are known as a relative measure of retardation of the dissolution process [36]. The variation of temperature in the system was monitored with time and the reaction number (RN) was calculated as in the following equation:

$$RN(°C/min) = \frac{(T_m - T_i)}{t_m}$$  \hspace{1cm} (11)

Where $T_m$ and $T_i$ are the maximum and initial temperature respectively, $t_m$ is the time in minutes taken to attain the maximum temperature.

The extent of corrosion inhibition can be expressed in terms of the percentage reduction in reaction number (%RR) given by the following equation [37].

$$%RR = \frac{RN_{uninhibited} - RN_{inhibited}}{RN_{uninhibited}} \times 100$$  \hspace{1cm} (12)

The thermometric parameters and inhibition efficiency are summarized in Table 7. The inhibition efficiency and $t_m$ increase with increasing inhibitor concentration.

The order of inhibition decreased in the order C3 > C5 > C4 > C2 > C1. This order is similar to that obtained from both gravimetric and gasometrical techniques.

3.2.6. Acidimetric measurements

The pH was checked for the five concentrations 50, 100, 150, and 200 ppm pre and post dipping in the checked solution for 7 hrs. only for the compound 3 as the most efficient inhibitor as obtained from all the previous used techniques.
Table 7. Thermometric parameters for the iron corrosion in acidic 1.0 M HCl solution for different concentrations of the studied sulfanyl pyridazine compounds as inhibitors.

<table>
<thead>
<tr>
<th>Inhibitor concentration ppm</th>
<th>$\Delta t_m$</th>
<th>$RN^{\circ}C/min$</th>
<th>Corrosion inhibition efficiency % $RR$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound no C5 C3 C4 C2 C1 C5 C3 C4 C2 C1 C5 C3 C4 C2 C1</td>
<td>50 271 228 219 210 124 0.036 0.054 0.078 0.086 0.093 80 78 75 74 73</td>
<td>100 301 253 246 239 136 0.032 0.049 0.056 0.064 0.067 86 83 81 78 77</td>
<td>150 335 281 273 265 151 0.029 0.045 0.05 0.058 0.06 90 86 82 80 79</td>
</tr>
</tbody>
</table>

The [H$^+$] value was computed in each case utilizing the next equation:

$$ pH = -\log[H^+] $$

(13)

The corrosion rate ($W$) of iron samples was computed utilizing the next equation:

$$ W (\text{mole} \cdot \text{dm}^{-3} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}) = \Delta H^+ / A t $$

(14)

Where $\Delta H^+$ is the variation between the first and last concentration of H$^+$, $A$ is the surface area of the coupon in cm$^2$ and $t$, the time in hrs. The $I.E.\%$ was computed utilizing the next equation:

$$ I.E.\% = 1 - \left( \frac{[\Delta H^+]_{inh}}{[\Delta H^+]_{uninh}} \right) \cdot 100 $$

(15)

Where $\Delta H^+_{inh}$ and $\Delta H^+$ are the changes in H$^+$ concentration in the presence and in the absence of the inhibitors, respectively.

The values of surface coverage ($\theta$) were computed utilizing the next equation: [39]

$$ \theta = 1 - \left( \frac{[\Delta H^+]_{inh}}{[\Delta H^+]_{uninh}} \right) $$

(16)

Table 8. Values of $I.E.\%$ from acidimetric method in 1.0 M HCl (at 30°C) for compound 3 as the most efficient inhibitor as obtained from all the previous used techniques.

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>$\Delta H^+ \cdot 10^4$</th>
<th>$\theta$</th>
<th>$I.E.%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>96</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>50</td>
<td>17</td>
<td>0.823</td>
<td>82.3</td>
</tr>
<tr>
<td>100</td>
<td>13</td>
<td>0.864</td>
<td>86.4</td>
</tr>
<tr>
<td>150</td>
<td>10</td>
<td>0.895</td>
<td>89.5</td>
</tr>
<tr>
<td>200</td>
<td>6</td>
<td>0.938</td>
<td>93.8</td>
</tr>
</tbody>
</table>

As follows from Table 8, the values of corrosion inhibition efficiency and surface coverage increased with increasing the inhibitor (C3) concentration due an increase in pH
and a decrease in the hydrogen ion concentration in the medium as the inhibitor molecule acts as a ligand for protons in acidic media.

3.3. Suggested corrosion inhibition mechanism

The corrosion inhibition mechanism in acidic medium is a blocking mechanism of action by adsorption of an inhibitor onto the metal surface. The adsorption of an inhibitor at the metal/solution interface is the first step in the inhibition mechanism in acidic media. Four types of adsorption may take place during inhibition involving organic molecules at the metal/solution interface [1, 18]:

1. Electrostatic attraction between charged molecules and the charged metal,
2. Interaction of unshared electron pairs in the molecule with the metal,
3. Interaction of π-electrons with the metal, and
4. A combination of the above.

Concerning inhibitors, the inhibition efficiency depends on several factors, such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface, and formation metal complexes [1, 40]. Physical adsorption requires the presence of both an electrically charged surface of the metal and charged species in the bulk of the solution; the presence of a metal having a vacant low-energy electron orbital and an inhibitor with molecules having relatively loosely bound electrons or a heteroatom with lone pair electrons. However, the compounds reported here can act by a blocking mechanism of action. They are protonated in an acid medium. Thus they become cations existing in equilibrium with the corresponding molecular form:

\[ \text{[Inhibit]} + x\text{H}^+ = \text{[Inhibit}_x]\text{H}^{x+} \quad (17) \]

The protonated inhibitor could be attached to the carbon steel surface by means of electrostatic interaction between Cl\(^{-}\) and a protonated inhibitor since the steel surface has positive charge in the HCl medium [1, 4, 18]. This could further be explained based on the assumption that in the presence of Cl\(^{-}\) the negatively charged Cl\(^{-}\) would attach to the positively charged surface and thereby the protonated inhibitor would be adsorbed onto the metal surface. Apart from electrostatic interaction, some chemical interaction is also involved. The non-bonding electrons of oxygen atoms and π-electrons of aromatic system cause chemical interaction. Compound 3 is initially adsorbed onto the metal surface and thereafter impedes corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic partial processes.

Conclusions

The following conclusions can be drawn from the previous discussion:

1. Sulfanyl pyridazine derivatives can be prepared easily from the corresponding ester in the pure form in good yields.
2. The results indicated that the tested compounds were promising corrosion inhibitors.
3. The corrosion inhibition efficiency increases with increasing inhibitor concentration and decreases with temperature.

4. The inhibition efficiency decreases in the following order: C3 > C5 > C4 > C2 > C1.

5. Compound 3 has high inhibition efficiency (93%) due to chelation with the steel metal surface and the inhibition is due to a blocking mechanism of action.

6. The inhibition is due to physicochemical adsorption of the used heterocyclic compound on steel surface, and the adsorption obeys the Langmuir isotherm.

7. The entropy of activation values are less negative for inhibited solutions than those for the uninhibited solutions. This suggests that an increase in randomness occurred while moving from the reactants to the activated complex.

8. The reduction in reaction number (RR%) and Δt_m increases with increasing inhibitor concentration, while the reaction number (RN) itself decreases with increasing inhibitor concentration.

9. All the analytical techniques used are efficient in determination of corrosion inhibition performance and corrosion inhibition mechanism of the inhibitors studied. The data obtained from different analytical techniques are in good agreement within (±2%).

10. The pH increases and the hydrogen ion concentration in the medium decreases upon addition of inhibitors as the inhibitor molecule acts as a ligand for protons in acidic media.

11. AAS showed that the addition of sulfanyl pyridazine inhibits the corrosion of steel in acidic environment and decreases the iron dissolution process (ferrous ion Fe^{+2} concentration) in acidic environment with lower pH value.

References


◆ ◆ ◆