Mercaptopropionic acid-modified oleic imidazoline as a highly efficient corrosion inhibitor for carbon steel in CO2-saturated formation water

Ziqi Zheng a, Junying Hu a,*, Noam Eliaz b, Li Zhou c, Xi Yuan c, Xiankang Zhong a, c

a State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China
b Department of Materials Science and Engineering, Tel-Aviv University, Ramat Aviv, Tel Aviv 6997801, Israel
c Research Institute of Natural Gas Technology, PetroChina Southwest Oil & Gasfield Company, Chengdu 610213, China

A R T I C L E   I N F O
Keywords:
Inhibitor
CO2 corrosion
Carbon steel
Adsorption
Molecular dynamics simulation
Quantum chemical calculation

A B S T R A C T
Two imidazoline derivatives (OI and MOI) were synthesized as highly efficient inhibitors, and their inhibition performances and mechanisms in CO2-containing solution were studied using weight loss measurements, electrochemical tests, surface analysis and theoretical calculations. The results indicate that OI and MOI show excellent inhibition efficiency. Especially for MOI, its inhibition efficiency is as high as 95.58% at 20 ppm. Theoretical calculations confirm that both inhibitors successfully adsorb on metal surface via chemisorption. MOI shows a better inhibition performance than OI, because the sulfhydryl in MOI can be used as a powerful adsorption site, effectively improving the adsorption ability of MOI.

1. Introduction

Corrosion poses a great threat to the safety of exploitation, transportation and storage of oil and gas. CO2 corrosion, known as sweet corrosion, is a common form of corrosion in the oil and gas industries, which is one of the main considerations in the application of carbon and low alloy steels [1–4]. Generally, for the same pH, the corrosiveness of H2CO3 is more severe than that of HCl or other strong acids [1,5,6]. Hence, it is very imperative to effectively alleviate the corrosion of steels in CO2-containing environments.

Adding corrosion inhibitor is one of the most widespread anti-corrosion measures because their addition can be implemented without disruption of a process, there is a wide variety of inhibitors to choose from depending on the environment and the metal to be protected, their utilization is relatively cheap but effective and they do not require significant operator expertise [7–10]. Some organic compounds have been used to curb the corrosion of carbon steel. This is because some heteroatoms (e.g., S, O and N) can form chemical bonds with the metal atoms. Consequently, protective films form on the metal surface.

Imidazoline and its derivatives are extensively used to control the corrosion of steels in CO2-containing condition because of their low toxicity and environmental friendliness [11,12]. However, imidazoline has shown some defects such as poor water solubility and easy hydrolysis [13], which seriously affects the inhibition performance of imidazoline. In order to improve the inhibition effect of imidazoline, the synergistic effect of imidazoline inhibitors and other compounds has been widely studied [14–18]. According to these studies, imidazolines was mixed with thiourea, L-cysteine, halogen ions and surfactants to improve their inhibition effect. Although this method can improve the corrosion inhibition effect and reduce the dosage of imidazolines, the improvement of their inhibition effect is very limited. This is mainly limited by the inhibition performance of imidazoline inhibitor used. Therefore, modifying the molecular structure of imidazoline inhibitors could be more effective in improving its inhibition performance.

It was reported that the inhibition performance of imidazolines is able to be improved by the introduction of suitable groups to their molecular structure [19–22]. These studies pay more attention to the influence of hydrophobic carbon chain length on imidazoline inhibition efficiency. There are few reports on the influence of substituents on imidazoline inhibition performance, especially those containing sulfur atoms. In addition, many studies reported [23–26] that sulfhydryl can show a strong ability to combine with metals through coordination bonds, significantly affect the adsorption ability of inhibitors. This is mainly due to the strong polarity property of sulfhydryl and the relatively high electronegativity of sulfur atom. The effect of sulfhydryl on the inhibition performance of imidazoline inhibitors has not been reported. Therefore, exploring the influence of sulfhydryl on the corrosion inhibition performance for imidazoline inhibitors will contribute to
better understand the relationship between the molecular structure of imidazoline inhibitors and their inhibition efficiency, which can also provide a theoretical basis for the development of new and efficient imidazoline inhibitors.

Mercaptopropionic acid has been widely used in pharmaceuticals [27], pesticides [28], and nanomaterials [29]. In the field of nanomaterials, for example, it has been used as a modifier to improve the stability and dispersion of quantum dots [29–32]. Kadian et al. [31] used mercaptopropionic acid to modify graphene quantum dots, which significantly improved their water solubility, fluorescence and quantum yield. Sukanya et al. [32] used mercaptopropionic acid to modify CdSe/CdS/ZnS, effectively enhancing their biocompatibility. Consequently, as a good modifier, mercaptopropionic acid was used to modify imidazoline inhibitor.

Oleic acid, which can be extracted from animals and plants, is characterized by wide sources, low price, environment-friendly and thermal stability. At the same time, the unsaturated long carbon chain in the molecular structure of oleic acid is also helpful to improve the inhibition performance of inhibitors [22]. In this work, oleic acid was used as a green raw material to synthesize oleic imidazoline (OI). Mercapto-oleic imidazoline (MOI) was developed by modifying OI with mercaptopropionic acid for the first time. The corrosion inhibition effect of OI and MOI on carbon steel in CO₂-saturated formation water was studied by weight loss measurements, electrochemical techniques and surface characterization. Quantum chemical calculations and molecular dynamics simulations were also used to unveil the inhibition mechanisms of the novel corrosion inhibitors.

2. Experimental section

2.1. Synthesis of corrosion inhibitors

Two imidazoline derivatives, OI and MOI, were synthesized as shown in Fig. 1. The synthesis procedures were as follows: i) 0.1 mol oleic acid, 0.12 mol tetraethylene pentamine and 30 mL dimethylbenzene (solvent) were added into the five-necked flask, ii) the mixture was heated at 160 °C for 4 h with stirring under N₂, then was further heated to 220 °C and reacted for 5 h, and iii) the solvent was removed in vacuo. Ultimately, a brownish liquid was obtained. During the whole synthesis process, N₂ gas was used to prevent oxidation of chemicals.

MOI was synthesized from OI as follows. First, 0.1 mol OI and 0.11 mol mercaptopropionic acid were added into the five-necked flask. The mixture was then stirred under reflux for 4 h. Next, the solvent was removed in vacuo. At last, a dark brown solid was obtained. N₂ gas was utilized during the synthesis process to prevent the oxidation of chemicals. The crude product was purified by column chromatography on silica gel.

2.2. Molecular structure characterisation

Molecular structure of OI and MOI was characterized using Fourier transform infrared spectrometer (FT-IR, WQF-520, Ruili, China). The ¹H NMR spectra of synthesized inhibitors were studied using a nuclear magnetic resonance spectrometer (NMR, Avance NEO 400, Bruker,
basically as follows (% wt): 0.65 Mn, 0.45 C, 0.20 Si, 0.17 Ni, 0.03 S, 0.15 Cr, 0.02 P, and balance Fe. The C content was determined using a Carbon-Sulfur Analyzer instrument (CS-3000, NCS Testing Technology Co., China), while the other elements were measured by Atomic Absorption Spectroscopy (iCE 300, Thermo Fisher Scientific, USA). The test solution, composed of 20.573 g/L NaCl, 1.335 g/L CaCl₂, 1.111 g/L NaHCO₃, 0.305 g/L MgCl₂, 0.044 g/L Na₂SO₄, was prepared from analytical reagents to simulate formation water. The pH of the CO₂-saturated formation water was 5.86.

2.4. Weight loss measurements

Samples were machined in following dimensions: 40 mm × 13 mm × 2.5 mm. All specimens were exposed to CO₂-saturated formation water with various concentrations of inhibitors for eight days at 60 °C. Before experiment, the samples were degreased with acetone, cleaned with absolute ethanol, dried in a N₂ gas flow, and weighed with an analytical balance. To evaluate reproducibility, three specimens were tested for each condition simultaneously. After immersion, remove the corrosion products on surface of specimen using a de-filming solution (10 g hexamethylenetetramine, 100 mL hydrochloric acid and 900 mL water). The corrosion rate (ν, mm/y) can be obtained by Eq. 1:

\[ \nu = \frac{87600 \times (w_1 - w_2)}{A \times \rho \times t} \]  

(1)

where \( w_1 \) and \( w_2 \) represent the weights before and after the experiment, respectively (g), \( A \) represents the surface area (cm²), \( \rho \) represents the density of the specimen (g/cm³), and \( t \) represents the experiment duration (h). The inhibition efficiency (\( \eta_r \), %) can be calculated using Eq. 2:

\[ \eta_r(\%) = \frac{\nu_0 - \nu_1}{\nu_0} \times 100 \]  

(2)

where \( \nu_0 \) and \( \nu_1 \) represent the corrosion rates of the samples in the solution without or with inhibitor, respectively.

2.5. Electrochemical measurements

All electrochemical measurements were carried out in a three-electrode cell. A platinum foil was used as the counter electrode (CE), a saturated calomel electrode was employed as the reference electrode (RE), and the sample was used as the working electrode (WE). The dimensions of all specimens are 10 mm × 10 mm × 5 mm. A copper wire was welded on one side of the specimen to provide electrical contact. Then, the specimen was sealed in epoxy. The exposed surface area of the entire test was performed in a CO₂-saturated solution. The inhibitor electrode cell. A platinum foil was used as the counter electrode (CE), and the sample was used as the working electrode (WE). The dimensions of all specimens are 10 mm × 2.5 mm. All specimens were exposed to CO₂-saturated formation water with various concentrations of inhibitors for eight days at 60 °C. Before experiment, the samples were degreased with acetone, cleaned with absolute ethanol, dried in a N₂ gas flow, and weighed with an analytical balance. To evaluate reproducibility, three specimens were tested for each condition simultaneously. After immersion, remove the corrosion products on surface of specimen using a de-filming solution (10 g hexamethylenetetramine, 100 mL hydrochloric acid and 900 mL water). The corrosion rate (\( \nu \), mm/y) can be obtained by Eq. 1:

\[ \nu = \frac{87600 \times (w_1 - w_2)}{A \times \rho \times t} \]

(1)

where \( w_1 \) and \( w_2 \) represent the weights before and after the experiment, respectively (g), \( A \) represents the surface area (cm²), \( \rho \) represents the density of the specimen (g/cm³), and \( t \) represents the experiment duration (h). The inhibition efficiency (\( \eta_r \), %) can be calculated using Eq. 2:

\[ \eta_r(\%) = \frac{\nu_0 - \nu_1}{\nu_0} \times 100 \]

(2)

where \( \nu_0 \) and \( \nu_1 \) represent the corrosion rates of the samples in the solution without or with inhibitor, respectively.

2.5. Electrochemical measurements

All electrochemical measurements were carried out in a three-electrode cell. A platinum foil was used as the counter electrode (CE), a saturated calomel electrode was employed as the reference electrode (RE), and the sample was used as the working electrode (WE). The dimensions of all specimens are 10 mm × 10 mm × 5 mm. A copper wire was welded on one side of the specimen to provide electrical contact. Then, the specimen was sealed in epoxy. The exposed surface area of the specimen was 1.0 cm². After being ground with SiC papers from grit 800 to 1200, the specimen was cleaned with ultrapure water and dried in a N₂ gas flow. Before the measurement, use CO₂ to purge the test solution for 120 min to deaerate. The purging of CO₂ gas was maintained throughout the test to ensure that the entire test was performed in a CO₂-saturated solution. The inhibitor was injected into the test solution after the deaeration was completed. The open circuit potential (OCP) was recorded for 1 h to reach a stable state. Electrochemical impedance spectra (EIS, CS310H, Corrtest, China) were acquired using a 5 mV amplitude sinusoidal wave in the frequency from 10⁻² to 10⁸ Hz. Polarization curves were acquired from −0.25−0.25 V vs. OCP with a scan rate of 1 mV/s.

Fig. 2 presents the FT-IR spectra of the two imidazoline inhibitors. The peaks at around 1655 and 1652 cm⁻¹ correspond to C=N bond which belongs to the imidazoline ring [40]. The peak at 1553 cm⁻¹ is attributed to the C=N bond [41]. The peaks at 2723 and 1367 cm⁻¹ correspond to −SH group and the C=O bond, respectively [42,43].
Corrosion Science 194 (2022) 109930

Fig. 3 shows the $^1$H NMR spectra of the two imidazoline inhibitors: (a) OI, (b) MOI.

Table 1

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Concentration (ppm)</th>
<th>Corrosion rate (mm/y)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>0.464 ± 0.009</td>
<td>—</td>
</tr>
<tr>
<td>OI</td>
<td>10</td>
<td>0.149 ± 0.003</td>
<td>68.95 ± 0.55</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.118 ± 0.006</td>
<td>75.50 ± 1.20</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.090 ± 0.003</td>
<td>81.21 ± 0.93</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.066 ± 0.007</td>
<td>86.26 ± 1.41</td>
</tr>
<tr>
<td>MOI</td>
<td>10</td>
<td>0.083 ± 0.005</td>
<td>82.70 ± 0.42</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.021 ± 0.002</td>
<td>95.58 ± 0.32</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.019 ± 0.001</td>
<td>96.08 ± 0.22</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.015 ± 0.003</td>
<td>96.79 ± 0.67</td>
</tr>
</tbody>
</table>

Fig. 3 shows the $^1$H NMR spectra of the two imidazoline inhibitors: OI (DMSO-$d_6$, 400 MHz): δ (ppm) = 5.32 (s, 2 H, −CH=CH−), 3.49 (s, 4 H, −N−CH$_2$−CH$_2$−N−), 3.08 (d, 2 H, −N−CH$_2$−), 2.69 – 2.47 (m, 12 H, −CH$_2$−CH$_2$−NH−), 2.33 (m, 2 H, −N==C−CH$_2$−), 2.01 (d, 4 H, −CH$_2$−CH=), 1.45 (s, 2 H, −NH$_2$), 1.27 – 1.23 (m, 24 H, −CH$_2$−CH$_2$−CH$_2$−), 0.86 (t, 3 H, −CH$_3$), MOI (CDCl$_3$, 400 MHz): δ (ppm) = 5.32 (s, 2 H, −CH=CH−), 3.65 (s, 4 H, −N−CH$_2$−CH$_2$−N−), 3.32 (s, 2 H, −N−CH$_2$−), 2.83 – 2.63 (m, 16 H, −CH$_2$−CH$_2$−NH−), 2.46 (m, 2 H, −N==C−CH$_2$−), 2.16 (s, 1 H, −NH−C==O), 1.99 (m, 4 H, −CH$_2$−CH=), 1.60 (s, 1 H, −SH), 1.35 – 1.18 (m, 22 H, −CH$_2$−CH$_2$−CH$_2$−), 0.86 (m, 3 H, −CH$_3$).

The results of $^1$H NMR and FT-IR spectra confirm that both OI and MOI inhibitors were successfully synthesized.

3.2. Corrosion inhibition performance

3.2.1. Weight loss measurements

Table 1 lists the corrosion rates of specimens exposed to the solution with various concentrations of inhibitors for eight days at 60 °C. The average corrosion rates of specimens in the blank solution is 0.46 mm/y, which is a relatively high corrosion rate for CO$_2$ corrosion. While, the addition of inhibitor, the inhibition efficiency increases with the increasing inhibitor concentration. The corrosion rate of the specimens in the solution with 100 ppm OI and 100 ppm MOI are 0.066 mm/y and 0.015 mm/y, respectively. This suggests that OI and MOI can likely adsorb on specimen surface. It is noteworthy that with 20 ppm MOI, the inhibition efficiency is as high as 95.58%, which is much higher than that with 20 ppm OI. Therefore, the modification of the imidazoline inhibitor by introducing sulfhydryl can improve the inhibition performance. Table 2 lists the comparison of the inhibition efficiency of MOI with other imidazoline derivatives in the literatures. It can be seen that, compared with other imidazoline derivatives in the literatures, MOI shows more excellent corrosion inhibition efficiency.

3.2.2. Electrochemical measurements

Fig. 4 shows the electrochemical impedance spectroscopy (EIS) plots for specimens exposed to various solutions at 60 °C. As can be seen from the Nyquist plots, the capacitive arcs are not normal semicircles, i.e., a not ideal capacitance behavior persists at the interface of solid and liquid [8,55,56]. Namely, it is not a pure capacitance [8]. Therefore, the constant phase element (CPE) usually stands for the capacitance [57]. The diameter of the capacitive arc enlarges remarkably in solution with inhibitors compared to blank solution, indicating that both OI and MOI...
can inhibit corrosion. In the Bode plots, the phase angle increases and widens when inhibitors are added, thus confirming the effective adsorption of inhibitors onto the specimen surface [58-60].

For quantitative analysis, the equivalent circuit models shown in Fig. 5 were used to fit the EIS data. In these equivalent circuits, the adsorption of inhibitors onto the specimen surface [58] widens when inhibitors are added, thus confirming the effective protection of the specimen surface by the inhibitors. In addition, the inhibition efficiency at each time point calculated from the evaluation of inhibitor performance. To evaluate it, the inhibition efficiency with 100 ppm MOI is significantly higher, namely 98.18%. Hence, the inhibition performance of OI modified with mercaptobenzimidazole is much higher than that in solution without inhibitors. This is due to the protection of the specimen surface by the inhibitors. In addition, the inhibition efficiency with 100 ppm OI is only 87.34%, while the inhibition efficiency with 100 ppm MOI is significantly higher, namely 98.18%. Hence, the inhibition performance of OI modified with mercaptobenzimidazole is significantly improved.

The stability over time of the inhibition effect is highly important for the evaluation of inhibitor performance. To evaluate it, the inhibition effect of 100 ppm inhibitor during 144 h soak exposed to the solution at 60 °C was determined via EIS measurements. Fig. 6 presents the inhibition efficiencies were maintained above 95% within 144 h.

Table 3 lists the fitting data of EIS. It is found that with inhibitor $R_{\text{tot}}$ is much higher than that in solution without inhibitors. This is due to the protection of the specimen surface by the inhibitors. In addition, the inhibition efficiency with 100 ppm OI is only 87.34%, while the inhibition efficiency with 100 ppm MOI is significantly higher, namely 98.18%. Hence, the inhibition performance of OI modified with mercaptobenzimidazole is significantly improved.

The stability over time of the inhibition effect is highly important for the evaluation of inhibitor performance. To evaluate it, the inhibition effect of 100 ppm inhibitor during 144 h soak exposed to the solution at 60 °C was determined via EIS measurements. Fig. 6 presents the inhibition efficiency at each time point calculated from $R_{\text{tot}}$. For OI and MOI, the inhibition efficiencies were maintained above 95% within 144 h. This indicates that OI and MOI can provide long-term stable and efficient protection of specimens in CO$_2$-containing environment. Compared with OI, MOI shows a higher inhibition efficiency at any time. Fig. 7 shows the polarization curves of the specimens exposed to various solutions. It is evident that both the cathodic and anodic current densities sharply reduce due to the addition of inhibitors. Namely, OI
and MOI can inhibit the anodic dissolution and the reduction of cathodic hydrogen ions at the same time. Therefore, both OI and MOI are classified as mixed-type inhibitors [10].

Table 4 lists the parameters of the polarization curves obtained from Tafel extrapolation. The inhibition efficiency ($\eta_p$, %) was calculated by Eq. 4:

$$\eta_p(\%) = \frac{i_{corr} - i_{corr}}{i_{corr}} \times 100$$

where $i_{corr}$ and $i_{corr}$ represent the corrosion current densities of specimens in uninhibited and inhibited formation water, respectively.

It can be found from Table 4, the inhibition efficiency at 100 ppm OI and 100 ppm MOI are 82.8% and 98.4%, respectively, suggesting that OI and MOI show good inhibition performance. The inhibition efficiency of MOI at 20 ppm is 95.6%, which is much greater than that of OI at the equal concentration. Like the results obtained from weight loss measurements, electrochemical measurement results also indicate that MOI shows a better inhibition effect compared to OI.

3.3. Adsorption thermodynamic and kinetic analysis

To further investigate the adsorption mechanism, the adsorption isotherms of OI and MOI were evaluated. The Langmuir adsorption isotherm [8,10,61] was successfully applied to describe the adsorption behaviors of OI and MOI:

$$\frac{c_{inh}}{\theta} = c_{inh} + \frac{1}{K_{ads}}$$

where $c_{inh}$ represents the concentration of the inhibitor (mg/L), $\theta$ represents the fractional surface coverage ($\theta = \eta_R$), and $K_{ads}$ represents the adsorption-desorption equilibrium constant (L/mg).

The standard free energy of adsorption ($\Delta G_{ads}$) was derived from Eq. 6 [62]:

$$\Delta G_{ads} = -RT \ln K_{ads}$$

where $R$ is the gas constant, and $T$ is the temperature.

![Fig. 5. The equivalent circuit models used to fit the EIS data: (a) in uninhibited solution, (b) in inhibited solution.](image)

![Fig. 6. The inhibition efficiency (based on $R_{tot}$) of 100 ppm inhibitors exposed to CO$_2$-saturated formation water at 60 °C within 144 h immersion.](image)

![Table 3](image)

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Concentration (ppm)</th>
<th>$R_s$ ($\Omega \cdot \text{cm}^2$)</th>
<th>CPEf $\gamma_0$ ($\Omega \cdot \mu\Omega \cdot \text{cm}^3$)</th>
<th>n</th>
<th>$R_t$ ($\Omega \cdot \text{cm}^2$)</th>
<th>CPEf $\gamma_0$ ($\Omega \cdot \mu\Omega \cdot \text{cm}^3$)</th>
<th>n</th>
<th>$R_{ct}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$R_{tot}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$\eta_R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>6.37</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>781</td>
<td>0.77</td>
<td>108.0</td>
<td>108.0</td>
<td>-</td>
</tr>
<tr>
<td>OI</td>
<td>10</td>
<td>7.83</td>
<td>246.3</td>
<td>0.75</td>
<td>0.4</td>
<td>9</td>
<td>0.69</td>
<td>354.7</td>
<td>355.1</td>
<td>69.59</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>6.65</td>
<td>251.4</td>
<td>0.81</td>
<td>259.8</td>
<td>2087</td>
<td>0.39</td>
<td>212.8</td>
<td>472.6</td>
<td>77.15</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6.60</td>
<td>71.2</td>
<td>0.92</td>
<td>6.5</td>
<td>256</td>
<td>0.63</td>
<td>575</td>
<td>581.5</td>
<td>81.43</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>6.65</td>
<td>244.7</td>
<td>0.80</td>
<td>636.1</td>
<td>3885</td>
<td>0.53</td>
<td>217.1</td>
<td>853.2</td>
<td>87.34</td>
</tr>
<tr>
<td>MOI</td>
<td>10</td>
<td>6.67</td>
<td>189.2</td>
<td>0.82</td>
<td>523.9</td>
<td>14190</td>
<td>0.88</td>
<td>147.1</td>
<td>671.0</td>
<td>83.90</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>6.54</td>
<td>150.5</td>
<td>0.84</td>
<td>1223.0</td>
<td>1958</td>
<td>0.68</td>
<td>512.7</td>
<td>1735.7</td>
<td>93.78</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6.59</td>
<td>105.7</td>
<td>0.86</td>
<td>2304.0</td>
<td>900</td>
<td>0.67</td>
<td>1109.0</td>
<td>3413.0</td>
<td>96.84</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>6.46</td>
<td>52.3</td>
<td>0.92</td>
<td>2577.0</td>
<td>874</td>
<td>0.49</td>
<td>3342.0</td>
<td>5919.0</td>
<td>98.18</td>
</tr>
</tbody>
</table>
\[ \Delta G_{\text{ads}} = RT \ln (1 \times 10^6 K_{\text{ads}}) \] (6)

where \( R \) and \( T \) represent the molar gas constant and the thermodynamic temperature, respectively, and \( 1 \times 10^6 \) represents the concentration of water (mg/L) [63].

As can be found from Fig. 8, the Langmuir adsorption isotherm is fairly consistent with the experimental data. Table 5 lists the calculated thermodynamic adsorption parameters of inhibitors. As can be found, the linear correlation coefficients \( (R^2) \) of OI and MOI are higher than 0.99, demonstrating that OI and MOI follow the Langmuir adsorption model. The \( \Delta G_{\text{ads}} \) values for OI and MOI are 40.04 kJ/mol and 50.03 kJ/mol, respectively. Generally, if \( \Delta G_{\text{ads}} > -20 \text{kJ/mol} \), the charged inhibitors are claimed to adsorb on metal surface by electrostatic interaction (physical adsorption) [8,64]; if \( \Delta G_{\text{ads}} < -40 \text{kJ/mol} \), the inhibitors are claimed to adsorb on the metal surface by forming coordinate covalent bonds (chemisorption) [8,65,66]. Therefore, in this work, OI and MOI are found to adsorb by chemisorption. Compared with physical adsorption, the film formed by chemisorption is stronger and more stable [67], i.e., OI and MOI show excellent inhibition performance. Furthermore, MOI shows a more negative \( \Delta G_{\text{ads}} \) value than OI, indicating that MOI forms stronger and more stable chemical bonds with the Fe atoms to slow down the corrosion [68].

In order to further investigate the kinetics of the corrosion reaction, potentiodynamic polarization measurements were conducted at 40–70 °C in the solution with or without 100 ppm inhibitor. The activation energy \( (E_a) \) was calculated by Eq. 7 [63]:

![Fig. 7. Potentiodynamic polarization curves of specimens exposed to both inhibited and uninhibited CO₂-saturated formation water at 60 °C: (a) OI, (b) MOI.](image1)

![Fig. 8. The Langmuir adsorption isotherms of inhibitors exposed to CO₂-saturated formation water at 60 °C.](image2)

![Fig. 9. Arrhenius plots of specimens exposed to CO₂-saturated formation water with and without 100 ppm inhibitors.](image3)

### Table 4
Fitted electrochemical parameters deduced from polarization curves for specimens exposed to both inhibited and uninhibited CO₂-saturated formation water at 60 °C.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Concentration (ppm)</th>
<th>( E_{\text{corr}} ) (V vs. SCE)</th>
<th>( i_{\text{corr}} ) (A/cm²)</th>
<th>( \eta_p ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>-0.753</td>
<td>2.5 \times 10^{-4}</td>
<td>-</td>
</tr>
<tr>
<td>OI</td>
<td>10</td>
<td>-0.687</td>
<td>6.9 \times 10^{-5}</td>
<td>72.40</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-0.696</td>
<td>6.1 \times 10^{-5}</td>
<td>75.60</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.718</td>
<td>4.9 \times 10^{-5}</td>
<td>80.40</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-0.692</td>
<td>4.3 \times 10^{-5}</td>
<td>82.80</td>
</tr>
<tr>
<td>MOI</td>
<td>10</td>
<td>-0.704</td>
<td>3.3 \times 10^{-5}</td>
<td>86.80</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-0.692</td>
<td>1.1 \times 10^{-5}</td>
<td>95.60</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.676</td>
<td>5.0 \times 10^{-6}</td>
<td>98.00</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-0.709</td>
<td>4.0 \times 10^{-6}</td>
<td>98.40</td>
</tr>
</tbody>
</table>

### Table 5
Thermodynamic parameters of inhibitors exposed to CO₂-saturated formation water at 60 °C.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Slope</th>
<th>Intercept ( (\text{mg/L}) )</th>
<th>( K_{\text{ads}} ) (L/mg)</th>
<th>( \Delta G_{\text{ads}} ) (kJ/mol)</th>
<th>Linear correlation coefficient, ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>OI</td>
<td>1.159</td>
<td>0.527</td>
<td>1.896</td>
<td>-40.04</td>
<td>0.999</td>
</tr>
<tr>
<td>MOI</td>
<td>1.018</td>
<td>0.014</td>
<td>69.93</td>
<td>-50.03</td>
<td>0.999</td>
</tr>
</tbody>
</table>
Table 6
Corrosion kinetic parameters for the carbon steel exposed to CO$_2$-saturated formation water with or without 100 ppm inhibitors.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$E_a$ (kJ/mol)</th>
<th>Linear correlation coefficient, $r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>25.16</td>
<td>0.986</td>
</tr>
<tr>
<td>OI</td>
<td>23.54</td>
<td>0.966</td>
</tr>
<tr>
<td>MOI</td>
<td>4.35</td>
<td>0.986</td>
</tr>
</tbody>
</table>

\[
\frac{i_{corr}}{i_{corr}} = A_{exp} \left( \frac{E_a}{RT} \right)^n (7)
\]

where $A$ represents the Arrhenius pre-exponential factor (or, frequency factor), $N_a$ represents Avogadro’s number, and $h$ represents Planck’s constant.

Fig. 9 presents the plot of ln($i_{corr}$) vs. 1/$T$. Table 6 lists the reaction kinetic parameters calculated. It is found that $E_a$ in the solution with inhibitors is smaller than that in the solution without inhibitors, which is mainly due to the strong chemisorption of inhibitors on the specimen surface [69].

3.4. Surface characterization

3.4.1. Surface morphology

Fig. 10 presents the surface morphologies (SEM images) of samples exposed to the solution at 60 °C for eight days, with or without 100 ppm inhibitors. It is evident that in the blank solution (Fig. 10a), significant non-uniform corrosion occurs on the specimen surface, with a large amount of corrosion products. In the inhibited solution (Fig. 10b,c), the sample surface is relatively smooth. Only little corrosion occurs, indicating that OI and MOI successfully inhibited corrosion. In the presence of MOI, the fine scratches produced during the grinding process can still be observed on the specimen surface, possibly indicating that MOI shows a better inhibition performance than OI.

3.4.2. Contact angle (CA) measurements

The hydrophobic surface film formed by adsorption of inhibitors has been reported to block the corrosion sites [8]. CA measurements can reveal the hydrophobic performance of this barrier [70]. Fig. 11 shows the CA between water drops and the surfaces of specimens pre-immersed in the blank solution at 60 °C for eight days. The CA on the specimens pre-immersed in the blank solution (Fig. 11a) is 40°. The low contact angle owes to the irregular corrosion products on the surface and rough corroded specimen surface [71]. The CA increases to 60° on the specimen pre-immersed in the OI-inhibited solution (Fig. 11b), and to 105° on the specimen pre-immersed in the MOI-inhibited solution (Fig. 11c). The increase in CA is probably ascribed to the adsorption of inhibitors [8,72].

3.4.3. XPS analysis

Fig. 12 shows the XPS high-resolution spectra acquired from the surfaces of specimens pre-immersed for eight days exposed to the solution at 60 °C, with or without 100 ppm inhibitors. From Fig. 12a, it is evident that the Fe 2p3/2 spectrum in the uninhibited solution consists of four peaks corresponding to Fe$_2$O$_3$ (710.7 eV), FeCO$_3$ (710.2 eV), FeO (709.3 eV) and FeOOH (711.8 eV) [73]. After immersion in the inhibited solutions, the FeO peak disappears, but a Fe peak appears (706.6 eV) [74]. This suggests that OI and MOI effectively inhibited the corrosion. The O 1 s spectrum (Fig. 12b) contains four peaks corresponding to Fe oxides (529.8 eV), –OH (531.5 eV), C=O (531.0 eV) and C–O/CO$_3^{2−}$ (532.6 eV) [75,76]. The C 1 s spectrum (Fig. 12c) contains two peaks corresponding to FeCO$_3$ (289.3 eV) and C–H/C–C (284.8 eV) [36,77] in the case of the uninhibited solution. In the inhibited solutions, a peak corresponding to C=O/C=O=O/S (285.6 eV) appears, proving the adsorption of inhibitors [78]. The N 1 s spectrum (Fig. 12d) contains two peaks, corresponding to N–Fe/–NH$_2$ (399.9 eV) and =N= (399.1 eV) [74,79]. The S 2p spectrum (Fig. 12e) contains two peaks corresponding to S–Fe (162.1 eV) and C–S–H (163.6 eV) [78,80]. Thus, XPS analysis clearly reveals that the two inhibitors successfully absorbed on surface of steel.

3.5. Quantum chemical calculations

3.5.1. Frontier molecular orbit (FMO)

The molecular structure of inhibitors was studied by quantum chemical calculations, employing DFT. It is well known that the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) determine the capacity of the molecule to accept electrons and provide electrons, respectively [81–83]. Fig. 13 presents...
the optimized molecular structures of the inhibitors and their distributions of HOMO and LUMO. As can be seen, the HOMOs of OI and MOI are mainly distributed around the imidazoline ring, indicating that this ring can provide electrons to Fe atoms. However, the distributions of LUMOs of the two inhibitors are significantly different. For OI, the LUMO is still distributed around the imidazoline ring, while for MOI, the LUMO is distributed around the sulfhydryl. In other words, OI and MOI can accept electrons from the Fe atoms through the imidazoline and sulfhydryl, respectively. It is worth noting that OI can only form covalent bonds and feedback bonds with the Fe atoms through a single imidazoline ring. In contrast, MOI adsorbs on the metal surface not only by providing electrons to Fe atoms through the imidazoline ring to form covalent bonds, but also by accepting electrons from Fe atoms through the sulfhydryl to form feedback bonds.

3.5.2. Electrostatic potential (ESP)

The ESP distribution on a molecule surface is usually used to predict electrophilic and nucleophilic reaction sites. It can further explain electrostatic interactions and predict reaction sites [84]. Fig. 14a,b shows the ESP distributions of the two inhibitors. The red color illustrates the positively charged regions, while the blue color suggests negatively charged regions. The orange and cyan spheres stand for the maxima and minima of the ESP points [36], respectively. Generally, the more positive ESP regions are considered preferable for attraction of nucleophilic species, while more negative ESP regions attract electrophilic species [85]. Furthermore, atoms near the extreme points of ESP are the most likely sites for chemical reaction. It can be seen that many extreme points are distributed around the imidazoline ring and the sulfhydryl. This suggests that the two regions are more inclined to undergo electrophilic (or nucleophilic) reactions with Fe atoms.

Fig. 14c,d shows the van der Waals surface area at various ESP intervals. It can be further used to quantitatively describe the distributions of ESP. It is evident that the area of the positively charged region increases after the OI is modified with mercaptopropionic acid. This may be due to the introduction of the sulfhydryl, which shows an electron-withdrawing effect.

3.6. GFN-xTB calculations

To clarify the adsorption mechanism of inhibitor molecules on Fe
surface, GFN-xTB method was used to calculate and determine the interaction between OI/MOI and Fe surface. Fig. 15 a,b shows the optimized adsorption configuration and electron density difference of OI and MOI on Fe (1 1 0) surface. It can be seen that, for the OI-Fe (1 1 0) adsorption system, the bond length between N atom in imidazoline ring and Fe atom ($r_{\text{cov(IM-N-Fe)}}$) is 1.875 Å. The bond lengths between N atoms in side chain and Fe atoms ($r_{\text{cov(Ch-N-Fe)}}$) are 2.033 Å and 2.152 Å respectively. The $r_{\text{cov(IM-N-Fe)}}$ is close to the sum of covalent radius of N atom and Fe atom ($r_{\text{cov(N-Fe)}}$) (the covalent radii of N and Fe atoms are 0.71 Å and 1.16 Å respectively) [86]. However, there is a big gap between the $r_{\text{cov(Ch-N-Fe)}}$ and $r_{\text{cov(N-Fe)}}$. This indicates that, the ability of bonding between N atoms in the side chain and Fe atoms is weak. Therefore, for OI, it is difficult to adsorb on Fe surface through N atoms in the side chain. This is in good agreement with the results of ESP and FMO. For the MOI-Fe (1 1 0) adsorption system, the bond lengths of N-Fe and S-Fe are 1.921 Å and 2.268 Å respectively. The bond lengths of N-Fe and S-Fe are close to the sum of covalent radii of N/S atoms and Fe atoms (the covalent radii of N, Fe and S atoms are 0.71 Å,1.16 Å and 1.03 Å, respectively) [86]. This suggests that MOI can adsorb on the Fe surface by N/S atoms.

Adsorption energy ($E_{\text{ads}}$) can be used to further measure the adsorption strength of inhibitors on the Fe surface. $E_{\text{ads}}$ can be obtained by the Eq. 8 [58]:

$$E_{\text{ads}} = E_{\text{total}} - (E_{\text{surf}} + E_{\text{inh}})$$

where $E_{\text{total}}$ represents the total energy of the adsorption system, $E_{\text{surf}}$ represents the energy of Fe (1 1 0) surface and $E_{\text{inh}}$ represents the energy of OI or MOI. The calculated $E_{\text{ads}}$ of OI and MOI are −500.51 kJ/mol and −713.94 kJ/mol, respectively. Furthermore, the $E_{\text{ads}}$ of MOI is more negative than that of OI, i.e., MOI has a stronger adsorption ability [37,83].

To determine the electron transfer between OI/MOI and Fe surface, the electron density difference ($\Delta \rho$) can be obtained by the Eq. 9 [73]:

$$\Delta \rho = \rho_{\text{inh/surf}}(r) - \rho_{\text{surf}}(r) - \rho_{\text{inh}}(r)$$

where $\rho_{\text{inh/surf}}(r)$, $\rho_{\text{surf}}(r)$ and $\rho_{\text{inh}}(r)$ represent the electron densities of the total adsorption system, the clean Fe (1 1 0) surface and isolated inhibitor molecule, respectively. Fig. 15c,d shows the difference of electron density for the adsorption of OI/MOI on Fe (1 1 0) surface. The isosurfaces of blue and green represent the deficiency and accumulation of electrons, respectively. It can be found that Fe atoms bonded with OI and MOI exhibit significant electron accumulation, while N atoms and S atom show obvious electron deficiency. This indicates that the adsorption of OI and MOI on the Fe (1 1 0) surface is mainly achieved by electron-donation of the bonded N and S atoms to Fe atoms [36].

Partial density of states (PDOS) can be used to further explore the interaction between OI/MOI and Fe surface [58,73,87]. Fig. 16 shows the PDOS for the 3d-orbitals of Fe atoms and valence electron orbitals of OI or MOI before and after adsorption. It can be seen that, after adsorption (Fig. 16c,d), there is a significant molecular orbital overlap between the 3d-orbital of Fe atoms and the energy gaps of OI and MOI, confirming the strong interaction between the OI/MOI and Fe surface [83].

3.7. Inhibition mechanism of imidazoline inhibitors

In the light of the experimental and theoretical calculations results, the inhibition mechanism of imidazoline inhibitors can be proposed. The $\Delta G_{\text{ads}}$ listed in Table 5 indicate that OI and MOI adsorb on the metal surface via chemisorption. According to XPS results, peaks of Fe–N and Fe–S are present in the N 1s and S 2p3/2 spectra, respectively. This also indicates that OI and MOI adsorb on the metal surface by forming chemical bonds (chemical adsorption) with Fe atoms. Quantum
chemical calculations illustrate that the HOMO and LUMO of MOI are distributed around the imidazoline ring and sulfhydryl group, respectively. In other words, MOI adsorbs not only by donating electrons to Fe atoms through the imidazoline ring to form covalent bonds, but also by accepting electrons from Fe atoms through the sulfhydryl group to form feedback bonds. For OI, both HOMO and LUMO are only distributed around the imidazoline ring, i.e., OI can only form covalent bonds and feedback bonds with the Fe atoms through the single imidazoline ring. In addition, the results of GFN-xTB confirm that N atom in imidazoline ring and S atom in sulfhydryl are effective adsorption sites.  

According to the literature [61,88,89], the sulfhydryl, used as a powerful adsorption active site, can show a strong ability to combine with metals through coordination bonds. This is mainly due to the fact that the S atom can transfer its unshared electron pairs to the d-orbitals of metal atoms on the surface. This can significantly improve the adsorption ability of inhibitors. The enhancement of adsorption capacity can make the inhibitor films more stable and difficult to fall off. This can provide a more long-term and effective protection for metals. Furthermore, OI and MOI can repel corrosive species by long hydrophobic carbon chains [12,90]. For MOI, the better inhibition performance is due to its own strong adsorption, which also enhances the hydrophobicity of the alkyl chains [90]. To sum up, sulfhydryl can effectively improve the corrosion inhibition performance of imidazoline inhibitors, which is of great significance for the construction of efficient imidazoline corrosion inhibitor.

4. Conclusions

In this work, two imidazoline derivatives, oleic imidazoline (OI) and mercapto-oleic imidazoline (MOI), were synthesized and studied as corrosion inhibitors for carbon steel in CO$_2$-saturated formation water. The following conclusions were drawn:

1. The high inhibition efficiency of two inhibitors is due to the fact that they can form chemical bonds with Fe atoms to slow down the corrosion. MOI shows an excellent inhibition efficiency – 95.58% at a very low concentration of 20 ppm. MOI also shows an outstanding adsorption stability, i.e., the prominent inhibition efficiency of MOI can be stably maintained without any decrease during 144 h immersion.

2. Theoretical calculations confirm that MOI has stronger adsorption ability. The sulfhydryl substituent in MOI can be used as a powerful adsorption active site, effectively improving the adsorption ability of MOI.

CRediT authorship contribution statement

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Junying Hu and Xiankang Zhong are grateful to the support from the National Natural Science Foundation of China (grant No. 51501160, and Scientific and Technological Innovation Team for the National Natural Science Foundation of China (grant No. 51501160, the work reported in this paper.

References


Fig. 16. PDOS plots of OI and MOI before (a, b) and after (c, d) absorbed on the Fe (1 1 0) surface: (a, c) OI, (b, d) MOI.

Acknowledgements

Junying Hu and Xiankang Zhong are grateful to the support from the National Natural Science Foundation of China (Grant No. 51501160, and Scientific and Technological Innovation Team for the National Natural Science Foundation of China (Grant No. 51501160, the work reported in this paper.

References


Fig. 16. PDOS plots of OI and MOI before (a, b) and after (c, d) absorbed on the Fe (1 1 0) surface: (a, c) OI, (b, d) MOI.

Acknowledgements

Junying Hu and Xiankang Zhong are grateful to the support from the National Natural Science Foundation of China (Grant No. 51501160, and Scientific and Technological Innovation Team for the National Natural Science Foundation of China (Grant No. 51501160, the work reported in this paper.

References
