Review article

A novel imidazoline derivative as corrosion inhibitor for P110 carbon steel in hydrochloric acid environment

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A novel imidazoline derivative, 2-methyl-4-phenyl-1-tosyl-4, 5-dihydro-1H-imidazole (IMI), was prepared and investigated as corrosion inhibitor for P110 carbon steel in 1.0 M HCl solution by weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests. The inhibition efficiency increased with the rising concentration of IMI inhibitor. The test results and fitting data indicated that the IMI behaved as a mixed-type inhibitor and obeys the Langmuir adsorption isotherm. Scanning electron microscopy (SEM) was carried out to investigate the surface of carbon steel specimens, showing great protection from aggressive solution. Finally, inhibition mechanism of IMI on metal surface was further discussed.

1. Introduction

To improve the productivity in the oil and gas industry, acidic stimulation techniques such as matrix acidizing and acid fracturing are widely used. In these processes, large amount of highly concentrated acid, such as hydrochloric acid (HCl) and hydrofluoric acid (HF), is used to dissolve carbonate minerals [1].

However, the application of acid fluids in development of oil and gas fields can easily lead to severe corrosion on metal equipment including downhole tools, metal tubular and drill pipes. As a consequence, the costs of equipment maintenance and the security risks both increase dramatically, which contributes to the great economic losses and decline of production efficiency.

To protect the metal tools exposed to acid medium in petroleum industry, several methods such as anti-corrosion coatings, corrosion inhibitors and corrosion resistant steel, have been developed. Among them inhibitor is one of the most effective process. In consideration of efficiency and cost, adding efficient inhibitors to corrosive media is one of the most important and valid methods to protect metal equipment in petroleum industry. Because it can dramatically reduce the corrosion rate even at a low concentration varying from 10 mg/L to 5000 mg/L [1].

The most widely used inhibitors in petroleum industry are imidazoline derivatives. In previous literature some efficient imidazoline inhibitors have been reported [2–5]. We have prepared IMI inhibitor at room temperature using cationic Br as initiator [6]. Then the target product was gained simply by heating the reaction system at reflux for 4 h (Scheme 1). The inhibitory performance of IMI as corrosion inhibitor for P110 carbon steel in 1.0M hydrochloric acid solution was investigated, using weight loss method, electrochemical technique. Scanning electron microscopy (SEM) was employed to analyze the protection behavior of IMI on the surface of P110 carbon steel.
2. Experimental

2.1. Reagents and materials

All chemicals used in this study were analytical reagent grade and purchased from Kelong Chemical Reagent Factory (Chengdu, China).

The corrosion test samples were P110 carbon steel containing (wt%): 0.26C, 0.19 Si, 1.37 Mn, 0.004 P, 0.004S, 0.028 Ni, 0.019 Cu, 0.013 Mo, 0.006 V, 0.062 Al and balanced Fe. The surfaces of these steel specimens were polished with different grades of emery papers and degreased in ethanol, rinsed with distilled water and then dried at room temperature. The aggressive solution of 1.0 M HCl prepared by the dilution of analytical grade HCl (37 wt%) with deionized water was used as a blank solution.

2.2. Synthesis and characterization of IMI

The imidazoline inhibitor IMI was synthesized according to the improved path (Scheme 1). The initial experiment was performed using styrene, NBS, acetonitrile, and tosyl ammonia at 25 °C. Then the intermediate was converted to imidazoline by heating the reaction system to 85 °C at reflux for 4 h. After the reaction was complete, saturated Na2S2O3 (50 mL) and NaHCO3 (50 mL) were added to quench it. The product was purified by flash column chromatography (dichloromethane/MeOH = 40:1) and then investigated by FT-IR and NMR spectroscopy.

2.3. Weight loss measurements

Triplicate specimens (22 mm × 12 mm × 2 mm) were immersed in 500 mL corrosive solution (1.0 M HCl solution) with varied concentration of IMI inhibitor at 60 °C for 72 h. After the test was completed, the samples were dipped in ethanol and washed with ultrasonic cleaner for several times followed by reweighting. The tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss was reported in 1–2% data errors.

2.4. Electrochemical measurements

Electrochemical measurements were carried out with a computer-controlled system CS310 (CorrTest Company, Wuhan, China) equipped with a standard three-electrode compartment. A saturated calomel electrode (SCE) coupled to a Luggin capillary was used as a reference electrode (RE), along with a platinum counter electrode as the auxiliary electrode (AE). The carefully treated P110 carbon steel was used as a working electrode (WE).

Before each EIS and polarization measurement, WE was immersed in 1.0 M HCl solution at 60 °C with and without different concentrations of inhibitors for 30 min to insure a steady open-circuit potential (OCP). In this situation, the response to the electrical excitation was determined only by the condition of the solid/liquid interface without any impact of electrode quality or other factors. All electrochemical measurements were repeated at least three times under the same condition so that repeatable data were guaranteed.

2.4.1. Potentiodynamic polarization measurements

With a scan rate of 1 mV/s, the potentiodynamic polarization curves were carried out in the potential range from −250 mV to 250 mV with reference to SCE at a steady open-circuit potential. The potentiodynamic current potential curves (Tafel curves) were simultaneously developed.

2.4.2. Electrochemical impedance spectroscopy measurements (EIS)

EIS measurements were performed at OCP in the wide frequency range from 100 kHz to 0.01 Hz at alternating current amplitude of 5 mV sine wave. Nyquist and Bode plots were analyzed to interpret the corrosion characteristics. A ZView3.0 version software was used to analyze and fit the impedance data.

2.5. Scanning electron microscope

The morphology of tested sample surfaces were carried out by SEM (JSM-7500F, Japan). The test was performed after the specimens was exposed to 1.0 M HCl solution for 72 h in the absence and presence of inhibitor IMI.

3. Results and discussion

3.1. FT-IR and NMR measurements

In order to characterize and confirm the product structure, FT-IR and 1H NMR spectroscopy test was performed. As shown in Fig. 1a and b, IR (cm⁻¹): 3275 (N–H), 2941 and 2876 (–CH₂–), 1656 and 1328 (C–N and C=C=N (imidazole ring)), 3063 and 814 (C–H (in benzene ring)), 1157 (C–SO₂–N). 1H NMR (400 MHz,CDCl₃): δ = 7.83 (d, 2H, benzene-H), 7.71 (d, 2H, benzene-H), 7.32 (m, 3H, benzene-H), 7.21 (d, 2H, benzene-H), 5.04 (dd,1H, imidazole-H), 3.29 (ddm, 2H, imidazole-H), 2.04 (s, 3H, benzene-CH₃), 1.61 (s, 3H, benzene-CH₃).

3.2. Weight loss measurements

The results of weight loss measurements for the corrosion of carbon steel in 1.0 M HCl with and without different inhibitor concentrations at 60 °C are shown in Table 1. The corrosion rate (v) was calculated by the following equation:

\[ v = \frac{W}{3t} \]

Scheme 1. The synthesis of imidazoline derivative IMI.
where $W$ is the average weight loss of parallel specimens, $S$ is the total area of one specimen, and $t$ is the immersion time. Subsequently, the inhibition efficiency ($\eta$) and surface coverage ($\theta$) of inhibitor IMI was calculated using the following equations:

$$
\eta(\%) = \frac{W_0 - W_{\text{inh}}}{W_0} \times 100\% \quad (2)
$$

$$
\theta(\%) = \frac{W_0 - W_{\text{inh}}}{W_0} \times 100\% \quad (3)
$$

where $W_0$ and $W_{\text{inh}}$ represent the weight loss of steel specimens in the absence and presence of IMI inhibitor, respectively.

Table 1

<table>
<thead>
<tr>
<th>C (mg L$^{-1}$)</th>
<th>$W$ (mg)</th>
<th>$S$ (cm$^2$)</th>
<th>$\nu$ (mg cm$^{-1}$ h$^{-1}$)</th>
<th>$\eta$ (%)</th>
<th>$\theta$ (%)</th>
</tr>
</thead>
<tbody>
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<td>blank</td>
<td>2072</td>
<td>6.634</td>
<td>4.150</td>
<td>–</td>
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<td>50</td>
<td>798.0</td>
<td>6.595</td>
<td>1.680</td>
<td>59.51</td>
<td>61.49</td>
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<td>100</td>
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<td>1.047</td>
<td>74.77</td>
<td>76.07</td>
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<td>168.8</td>
<td>6.613</td>
<td>0.3544</td>
<td>91.46</td>
<td>91.86</td>
</tr>
<tr>
<td>200</td>
<td>144.3</td>
<td>6.576</td>
<td>0.3048</td>
<td>92.66</td>
<td>93.04</td>
</tr>
<tr>
<td>250</td>
<td>156.4</td>
<td>6.602</td>
<td>0.3289</td>
<td>92.07</td>
<td>92.45</td>
</tr>
<tr>
<td>300</td>
<td>112.0</td>
<td>6.614</td>
<td>0.2351</td>
<td>94.34</td>
<td>94.60</td>
</tr>
</tbody>
</table>

The inhibition efficiency of IMI inhibitor increased with the increasing inhibitor concentrations, suggesting stronger adsorption layer and protection of inhibitor molecules on the metal surface with higher concentration of inhibitor. Table 1 shows the inhibition efficiency of 150 mg L$^{-1}$ IMI is greater than 90%.

3.3. Potentiodynamic polarization measurements

The potentiodynamic polarization curves for P110 carbon steel in 1.0 M HCl without and with various concentrations of IMI inhibitor at 60 °C are shown in Fig. 2, where remarkable decrease in corrosion rates, large displacements of both anodic and cathodic curves toward lower current densities and significant shifts in the corrosion potential $E_{\text{corr}}$ to more positive values are observed. These phenomena, which are more pronounced with the increase of IMI inhibitor concentration, indicate that anodic metal dissolution and cathodic hydrogen evolution processes are largely controlled by the barrier layer formed by IMI inhibitor molecules. The shape of potentiodynamic polarization curves in the inhibited solutions significantly changed with respect to those in the blank solution, suggesting that the corrosion processes on steel surfaces were deeply affected by IMI inhibitor [7–9].

The polarization parameters such as corrosion potential ($E_{\text{corr}}$) and corrosion current density ($I_{\text{corr}}$) obtained from the extrapolation of anodic and cathodic Tafel lines [10,11] are provided in Table 2, where the inhibition efficiency ($\eta_p$) of IMI inhibition were calculated by Equation (4).

$$
\eta_p = \frac{I_{\text{corr}} - I_{\text{corr,inhib}}}{I_{\text{corr}}} \times 100\% \quad (4)
$$

where $I_{\text{corr}}$ and $I_{\text{corr,inhib}}$ represent the values of corrosion current density for P110 carbon steel immersed without and with various concentrations of IMI inhibitor, respectively. In the presence of IMI inhibitor, the displacements of corrosion potential, varying from 9.47 to 30.19 mV, are far less than 85 mV compared with that of the blank solution. Hence, IMI inhibitor can be defined as mixed-type corrosion inhibitor [12]. As the inhibitor concentration increases, the value of $I_{\text{corr}}$ reduces sharply from 749.8 to 23.36 μA cm$^{-2}$ and the calculated
inhibition efficiency rise significantly, ending up with a maximum value of 96.99%.

This findings indicate the protection from aggressive solution may significantly influence the coverage rate of compound molecules on metal surface. The inhibition efficiencies calculated from the polarization tests present the same trend as those obtained from the weight loss measurements.

3.4. Electrochemical impedance spectroscopy (EIS)

The inhibition behavior of IMI inhibitor on P110 carbon steel immersed in 1.0M HCl at 60 °C were measured by EIS. The Nyquist plots of WE in aggressive solutions in the absence and presence of inhibitors are shown in Fig. 3. Evidently, the addition of IMI inhibitor didn’t change the shape of these plots, i.e., IMI inhibitor controlled the activity of the corrosion reaction rather than transformed its nature [13]. On the other hand, the electrochemical impedance was significantly affected by the addition of IMI inhibitor to the testing solution. Compared with the blank test, the diameters of the semicircles in the Nyquist plots increase with the increasing concentration of IMI inhibitor. In accordance with the former measurement, these results indicate the formation of IMI molecules layer on the metal surface, along with the subsequent protection properties [14–16].

The bode diagrams and phase angle curves for P110 carbon steel in 1.0 M HCl without and with various concentrations of IMI inhibitor are displayed in Fig. 4. Inhibition performance of IMI is notable according to the impedance values in the low frequency range and the increasing absolute impedance values demonstrate the high inhibition efficiency (Fig. 4a). Based on shifting trend of phase the angle plots (Fig. 4b), raising the concentration of IMI inhibitor contributes to more negative values of the phase angle, indicating the better inhibition ability of IMI with higher concentrations.

The obtained impedance data were fitted into the equivalent circuit (Fig. 5), using the CorrView-Electrochemistry Software. Based on the above results, R (QR) is suitable model for the Nyquist plot of specimen in blank solution while R (Q (R (QR))) is suitable for those immersed in aggressive solutions. In these equivalent circuits, $R_s$ represents the solution resistance, $R_f$ represents the film resistance and $R_{ct}$ represents the charge transfer resistance ($R_{ct}$). CPE is a constant phase element introduced to compensate for heterogeneity in the solution system [17]. $CPE_{dl}$ is a constant phase element, representing the double layer capacitance of the interface between carbon steel and solution [18]. Related parameters and corresponding data from electrochemical impedance spectroscopy measurements are listed in Table 2. The inhibition efficiency ($\eta_i$) was calculated according to the following equation:

<table>
<thead>
<tr>
<th>Conc. (mg L$^{-1}$)</th>
<th>$E_{corr}$ (mV vs SCE)</th>
<th>$I_{corr}$ (µA cm$^{-2}$)</th>
<th>$\eta_i$ (%)</th>
<th>$R_{ct}$ (Ω cm$^{-2}$)</th>
<th>CPE$_{dl}$ (µF cm$^{-2}$)</th>
<th>$\eta_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>−442.8</td>
<td>749.8</td>
<td>−</td>
<td>47.76</td>
<td>−</td>
<td>81.94</td>
</tr>
<tr>
<td>50</td>
<td>−433.3</td>
<td>97.37</td>
<td>87.01</td>
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<td>−427.1</td>
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<td>282.0</td>
<td>84.35</td>
<td>83.06</td>
</tr>
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<td>94.45</td>
<td>458.3</td>
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</tr>
<tr>
<td>200</td>
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<td>96.51</td>
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<td>91.87</td>
</tr>
<tr>
<td>250</td>
<td>−414.3</td>
<td>23.80</td>
<td>96.83</td>
<td>615.0</td>
<td>51.66</td>
<td>92.23</td>
</tr>
<tr>
<td>300</td>
<td>−412.6</td>
<td>23.36</td>
<td>96.88</td>
<td>890.7</td>
<td>47.96</td>
<td>94.64</td>
</tr>
</tbody>
</table>

Fig. 3. Nyquist plots for P110 carbon steel electrode obtained in 1.0M HCl solution containing various concentrations of IMI inhibitor at 60 °C.

Fig. 4. The Bode (a) and phase angle (b) plots for P110 carbon steel electrode in 1.0 M HCl solution in the absence and presence of different concentrations of IMI inhibitor at 60 °C.
on the metal surface is highly expected a straight line with the slope and the linear correlation coefficient close to 1, indicating that the adsorption of IMI inhibitor on the metal surface is illustrated in Fig. 8. There are at least two predominant adsorption models between the IMI inhibitor molecules and the metal surface: (i) interaction between the delocalized pi-electrons of benzene ring and the unoccupied d-orbital of Fe atoms [22–25]; (ii) donor—acceptor interactions between the lone electron pairs in heteroatoms (N and O) and the vacant d-orbital of the metal surface atoms [25–29]. These active adsorption (ΔC_ads) is calculated by the following expression [19]:

\[
\Delta C_{ads} = -RT\ln(55.5K_{ads})
\]

where \( R \) (J mol\(^{-1} \) K\(^{-1} \)) is the ideal gas constant, \( T \)(K) is the thermodynamic temperature and 55.5 (mol dm\(^{-3} \)) is the molar concentration of water in solution and. According to the above equations, values of \( K_{ads} \) and \( \Delta C_{ads} \) for IMI are \( 9.16 \times 10^4 \) L mol\(^{-1} \) and \(-28.34 \) kJ mol\(^{-1} \) respectively. The high value of \( \Delta C_{ads} \) indicates strong absorption between IMI inhibitor molecules and metal surface [20].

3.6. Surface analyses

Surface analyses for the corrosion of carbon steel specimens in 1.0 M HCl solution with and without inhibitors were carried out by SEM. Fig. 7 represents the morphologies of metal specimens immersed in aggressive solutions in the absence and presence of IMI at various concentrations.

The bumpy surface (Fig. 7A) with several corrosive pits shows that the steel specimen is seriously damaged by the aggressive solution. In contrast, the steel sample (Fig. 7B) with 100 mg/L of inhibitor IMI is less rough as well as sample (Fig. 7C) with a higher concentration of IMI. Moreover, the specimen (Fig. 7D) under the protection of IMI at 300 mg/L shows extremely smooth polishing scratches reflecting light. According to these findings, we can conclude that the key factor of protection against corrosion may be the formation of the adsorbed inhibitor molecules layer on surfaces of the metal specimens.

3.7. Mechanism of corrosion inhibition on the carbon steel

Generally, inhibitory performance of small organic molecules are known to originate from the formation of protective film absorbed on the metal surface [21]. Both the weight loss measurements and potentiodynamic polarization measurements revealed that the corrosion on carbon steel was significantly reduced in the presence IMI inhibitor. Furthermore, the adsorption isotherm analyses demonstrate that the adsorption of the inhibitor IMI on the metal surface is highly fitted to the Langmuir adsorption model. Moreover, the adsorption behavior of the protective film is mainly determined by the electrostatic interaction between the heteroatoms and multiple bonds of inhibitor molecules and the metal surface.

More specifically, the interaction between IMI inhibitor and metal surface is illustrated in Fig. 8. There are at least two predominant adsorption models between the IMI inhibitor molecule and metal surface: (i) interaction between the delocalized π-electrons of benzene ring and the unoccupied d-orbital of Fe atoms [22–25]; (ii) donor—acceptor interactions between the lone electron pairs in heteroatoms (N and O) and the vacant d-orbital of the metal surface atoms [25–29]. These active
electrons are prone to be shared with the vacant d-orbitals of the Fe atom. Hence, the above mechanism basically demonstrated the absorption behavior of IMI inhibition on carbon steel surface in 1.0 M HCl medium.

4. Conclusions

The corrosion inhibitor performance of synthesized IMI as corrosion inhibitor for P110 carbon steel in 1.0 M HCl solution has been evaluated and the main conclusions are as follows:

(1) IMI acts as excellent inhibitor for P110 carbon steel in 1.0 M HCl solution at 60 °C and the efficiency rises with the increasing concentration.
(2) According to the polarization measurements, IMI inhibitor can be defined as an excellent mixed-type inhibitor.
(3) Concluded from the weight loss measurements, the adsorption behavior of IMI inhibitor on metal surface obeys the Langmuir adsorption model.
(4) The SEM analysis indicates that the addition of IMI into the aggressive solution can remarkably protect carbon steel material from a macroscopic perspective.

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