Novel Inhibitors Containing Multi-Functional Groups for Pipeline Corrosion Inhibition in Oilfield Formation Water

Huiwen Tian* and Y. Frank Cheng‡,*

ABSTRACT
In this work, two novel inhibitors containing multi-functional groups were developed, and their inhibition performance for corrosion of X65 pipeline steel in CO2-saturated oilfield formation water was investigated using electrochemical measurements, surface characterization, and scanning vibrating electrode technique. Moreover, the inhibitors and the inhibition mechanism were further investigated by electrochemical quartz crystal microbalance and x-ray photoelectron spectroscopy. The inhibitors are able to decrease the corrosion rate of the steel in the solution by over 100 times at a concentration of \(3.2 \times 10^{-3}\) M, and the inhibition efficiency can exceed 98% for each inhibitor. The inhibitors are mixed-type ones, reducing both anodic and cathodic current densities, while the corrosion potential remains essentially constant. Corrosion inhibition is attributed to the formation, on the surface, of a film that consists of an insoluble complex containing inhibitor film and ferrous scale. The corrosion inhibition of the added inhibitor is more effective for the corroded electrode than for the freshly prepared steel electrode. This is attributed to the formation of the complex film by reactions of the inhibitor molecules and the pre-formed corrosion scale, and this film is more effective than the adsorptive inhibitor film for corrosion inhibition.

KEY WORDS: CO2 corrosion, inhibitors, multi-functional groups, oilfield formation water, pipelines

INTRODUCTION
Carbon steels are used as the key engineering materials in oil/gas and pipeline industries. However, carbon steels are prone to corrosion in aqueous environments containing dissolved carbon dioxide (CO2), which is a naturally occurring or intentionally injected constituent in oil and gas production, especially in produced brines containing aggressive ions such as chloride ions (Cl−). Moreover, the corrosion of carbon steel pipelines can be accelerated in the presence of organic acids such as acetic acid, which is commonly present in oilfield brines. The authors’ previous work showed that, in the presence of trace amount of acetic acid, the corrosiveness of the oilfield formation water is enhanced dramatically.

Application of various organic compounds, usually those containing nitrogen, sulfur, and oxygen heteroatoms in polar functional groups, as corrosion inhibitors has been effective to protect steels from corrosion in oilfield brines. Typically, imidazoline derivatives have been widely used as corrosion inhibitors in CO2 environments resulting from their strong tendency to adsorb on steel surface, forming a protective barrier against corrosion. However, imidazolines, as cationic surfactants, can aggravate localized corrosion by creating a number of micro-anodes, leading to local anodic dissolution. As a result, pitting corrosion occurs on pipelines when imidazoline inhibitors are added in the fluid.

Inhibitors containing functional groups such as amino, triazole, thiadiazole, thiol, furan, or acylhydrazone have been proven to be highly effective to inhibit...
steel corrosion in acids or brines. However, to date, there has been limited effort to integrate these functional groups into a single inhibitor molecule structure, attempting to improve and maximize the inhibitor performance.

In this work, two types of novel corrosion inhibitors were processed by integration of multi-functional groups and optimization of the prepared molecular structures, which are, therefore, expected to be highly effective for CO₂ corrosion inhibition in oilfield formation water. The inhibition performance was evaluated by electrochemical and micro-electrochemical measurements, including electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curves, and scanning vibrating electrode technique (SVET). The inhibitor molecules were characterized by electrochemical quartz crystal microbalance (EQCM) and x-ray photoelectron spectroscopy (XPS). The corrosion morphology was observed by scanning electron microscope (SEM). The inhibition mechanism of the developed inhibitors, especially the formation and growth of the adsorptive inhibitor film on the steel, was studied and analyzed. It is anticipated that this work will provide a promising insight into the development of novel inhibitors for effective corrosion control of pipelines in oil production.

**EXPERIMENTAL PROCEDURES**

**Inhibitors, Steel Specimen, and Solution**

The inhibitors were designed and prepared for the first time in the authors’ laboratory, with the processing procedure detailed in Figure 1, where the molecular formula of the two inhibitors, named as FATA and FTDA, were also included. All chemicals used were analytical grade.

Specimens used in this work were made from a sheet of API X65 steel plate, with a chemical composition (wt%): C 0.04, Si 0.2, Mn 1.5, P 0.011, S 0.003, Mo 0.02, and Fe balance. The specimen was cut into a cylinder and embedded into epoxy resin with an exposed surface area of 1 cm². The work face was ground up to
1000 grit silicon carbide paper, rinsed with deionized water, and degreased in acetone.

Test solution was prepared to simulate the oilfield formation water, with the chemical composition shown in Table 1. The solution contained NaHCO₃ 0.504 g/L, Na₂SO₄ 0.426 g/L, KCl 2.235 g/L, MgCl₂ 2.945 g/L, CaCl₂ 17.316, and NaCl 90.383 g/L. The concentration of acetic acid added in the test solution ranged from 3.2 × 10⁻³ M, which was consistent with the work conducted previously. The concentration of inhibitors added in the solution ranged from 3.2 × 10⁻⁵ M to 3.2 × 10⁻³ M. Prior to testing, the solution was deoxygenated by purging CO₂ (99.95%) for 4 h, and maintained throughout the test. The solution pH was 5.18. All tests were performed at 60°C, which was similar to the actual operating condition for gathering lines in oilfields.

**TABLE 1**

<table>
<thead>
<tr>
<th>Ions</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
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</thead>
<tbody>
<tr>
<td>Concentration (mg/L)</td>
<td>35,820</td>
<td>1,152</td>
<td>749</td>
<td>6,235</td>
<td>69,222</td>
<td>288</td>
<td>353</td>
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</tbody>
</table>

**Conventional Electrochemical Measurements**

Electrochemical measurements were conducted using a Solartron 1280°C electrochemical system on a three-electrode cell, where the steel specimen was used as working electrode, a platinum plate as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. After immersing in the test solution for 1 h, the open circuit potential of the steel achieved a steady state. The EIS was then measured with a sinusoidal excitation potential of 10 mV in the frequency range from 20 kHz to 10 mHz. The inhibition efficiency, ηₑᵣᵢᵣ, obtained from the EIS results was calculated by:

\[
\eta_{e蕊} = \frac{R_{ct} - R_{et}^0}{R_{ct}} \times 100\%
\]

where \(R_{ct}\) and \(R_{et}^0\) are charge-transfer resistances in the presence and absence of inhibitor in the solution, respectively.

After EIS measurements, the potentiodynamic polarization curve was measured at a potential sweep rate of 1 mV/s. The obtained inhibition efficiency, \(\eta_{et}\%), was calculated by:

\[
\eta_{et} = \frac{i^{corr}_{et} - i^{corr}}{i^{corr}} \times 100\%
\]

where \(i^{corr}\) and \(i^{corr}_{et}\) are corrosion current densities of the steel with and without addition of the inhibitor in the solution, respectively. The corrosion current density was derived from the measured polarization curves by Tafel extrapolation method.

To ensure the reproducibility of the testing results, each test was repeated at least three times. The mean value and the standard deviation were included for each data point, which was included in the tables listing the measured and derived electrochemical polarization and impedance parameters.

**Scanning Vibrating Electrode Technique Measurements**

The SVET measurements were conducted through a PAR M370 scanning electrochemical workstation, where a Pt/Ir (80%/20%) microprobe with a 10 μm tip was vibrated above the steel electrode with an amplitude (d) of 30 μm and a vibrating frequency of 300 Hz. The microprobe was located 100 μm above the electrode, which was mounted horizontally facing upward. A video camera connected to an optical microscope was used to monitor the position and movement of the microprobe during testing. The potential difference (ΔE) of the microprobe when it was located at the vibrating peak and the valley was measured by an electrometer incorporated in the scanning electrochemical workstation. The conductivity (k) of the solution was measured, and the solution resistance (Rₛ) between the vibrating peak and the valley was determined by Rₛ = d/k. The current was then obtained by I = ΔE/Rₛ.

**Scanning Electron Microscope Observation**

The surface morphology of the steel electrode after corrosion testing in solutions with and without inhibitor addition was characterized by a SEM (JEOL JSM-5600*).

**Electrochemical Quartz Crystal Microbalance Measurement**

Preparation of rotating EQCM electrodes and their characterization were described elsewhere previously. A 10 MHz cut quartz crystal with a sensitivity factor of 0.217 Hz cm²/νg was contained in exchangeable holders mounted on a rotating shaft. A 1 μm thick Fe electrode was prepared by electrodeposition (current density 20 mA/cm², 350 g/dm³ ferrous ammonium sulfate solution, pH 3.5) on a 190 mm thick sputter-deposited Au film, with an adhesion layer of 30 nm Cr. The prepared inhibitors were added into the test solution to reach a concentration of 10⁻³ M.

The frequency change, \(Δf\), is given with respect to the absolute resonant frequency of the quartz crystal, and contains two contributors:

\[
Δf = Δf_{m,ads} + Δf_η
\]

where \(Δf_{m,ads}\) is the mass dependent frequency shift resulting from adsorbing species on the electrode, and \(Δf_η\) is the concentration dependent frequency shift.
resulting from the viscosity change in the electrolyte sensed by EQCM. The effect of $\Delta f_\eta$ on EQCM signals is important only when the concentration of the adsorptive species is above $10^{-2}$ M. As the inhibitor concentration in this work was between $3.2 \times 10^{-5}$ M and $3.2 \times 10^{-3}$ M, the contribution of $\Delta f_\eta$ is thus not important. The obtained $\Delta f$ refers to $\Delta f_{m,ads}$ only.

X-Ray Photoelectron Spectroscopy Measurements

Analysis of surface film formed on the steel electrode was performed on a PHI 5700† XPS using the Al K$_\alpha$ radiation as the excitation source (1,486.6 eV). The energy of the emitted photoelectrons was analyzed with a hemispherical electron analyzer operating at pass energies of 29.3 eV and 58.7 eV for high-resolution spectra, and 187.8 eV for survey spectra. The spectra were measured at a base pressure below $2 \times 10^{-10}$ mbar ($2 \times 10^{-8}$ Pa). Two photoelectron emission angles ($\theta$), namely 5° (emission along the surface normal) and 90°, were utilized. For specimens with an inhomogeneous depth, the spectra measured at different take-off angles differ as a result of the different analysis depths. The analyzed depth by XPS is a function of the take-off angle, i.e., $3\lambda\sin\theta$, where $\lambda$ is the inelastic mean free path for electrons. The radius of the analyzed area was about 0.4 mm. The energy scales and possible charging effect were corrected using C1s peak at a binding energy of 284.6 eV.

RESULTS AND DISCUSSION

Polarization Curve Measurements and Analysis

The potentiodynamic polarization curves measured on X65 steel electrode in the test solution with various concentrations of FATA and FTDA inhibitors, respectively, are shown in Figure 2. Electrochemical parameters fitted from the polarization curves are listed in Table 2. It is seen that the addition of inhibitors in the solution decreases the corrosion rate of the steel remarkably. While both anodic and cathodic polarization curves are shifted left in inhibitor-containing solutions, i.e., both anodic and cathodic current densities decrease at individual potential compared to those measured in the inhibitor-free solution, the corrosion potential remains almost unchanged. The corrosion current density decreases substantially, with the inhibition efficiencies up to 99.2% and 98.6% in solutions containing $3.2 \times 10^{-3}$ M of FATA and FTDA, respectively. The developed inhibitors can be considered as mixed-type inhibitors that reduce both anodic and cathodic current densities. The unchanged corrosion potential, upon addition of inhibitors in the solution, is assumed that the inhibitors in the solution result in a blocking effect on both anodic and cathodic areas by forming an adsorptive inhibitor film. As multiple adsorption groups, such as aminotriazole, thiadiazole, thiol, furan, and acylhydrazone, are contained in the two inhibitor molecules, both FATA and FTDA are able to adsorb on the anodic and cathodic areas, thereby forming a barrier layer to inhibit both anodic and cathodic reactions. As a result, both anodic and cathodic Tafel slopes are increased. As the corrosion potential does not change obviously, the effect of the inhibitors on anodic and cathodic reactions are approximately identical.19

A conceptual model was developed in authors’ previous work to illustrate corrosion of pipeline steels exposed to CO$_2$-saturated oilfield formation water in the presence of acetic acid.5,15 The anodic reactions contain the dissolution of iron (Fe $\rightarrow$ Fe$^{2+}$ + 2e) and the formation of FeCO$_3$ scale (Fe + HCO$_3^-$ $\rightarrow$ FeCO$_3$ + H$^+$ + 2e), which deposits on the steel surface. Reduction of

![Figure 2](https://example.com/fig2.png)

**FIGURE 2.** Potentiodynamic polarization curves measured on X65 steel electrode in the test solution with various concentrations of FATA and FTDA inhibitors, respectively, where "Blank" means the inhibitor-free solution.
and FTDA inhibitors, respectively. It is seen that the solutions containing various concentrations of FATA corrosion potential after 24 h of immersion in the Bode plots measured on X65 steel electrode at its FeCO₃. It is noted that, when the inhibitor is present, concentration to 3.2×10⁻³ as seen in Table 2. A further increase of the inhibitor scale formation.

rather than the chemical mechanism, dominates the although the scale can be formed in inhibitor-containing solutions, the electrochemical mechanism, rather than the chemical mechanism, dominates the scale formation.

Electrochemical Impedance Spectroscopy Measurements and Analysis

Figures 3 and 4 show the Nyquist diagrams and Bode plots measured on X65 steel electrode at its corrosion potential after 24 h of immersion in the solutions containing various concentrations of FATA and FTDA inhibitors, respectively. It is seen that the size of the high-frequency semicircle in the Nyquist diagrams becomes bigger upon the addition of inhibitors in the solution, and further increases with the increasing inhibitor concentration. Because the

![Nyquist diagrams measured on X65 steel electrode at its corrosion potential after 24 h of immersion in the solutions containing various concentrations of (a) FATA and (b) FTDA inhibitors, respectively.](image)

![Bode plots measured on X65 steel electrode at its corrosion potential after 24 h of immersion in the solutions containing various concentrations of (a) FATA and (b) FTDA inhibitors, respectively.](image)

<table>
<thead>
<tr>
<th>Concentration (mol/L)</th>
<th>$i_{corr}$ (μA/cm²)</th>
<th>$E_{corr}$ (V SCE)</th>
<th>$i_{a}$ (mV/dec)</th>
<th>$i_{b}$ (mV/dec)</th>
<th>$η_{in}$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>138.2±2.3</td>
<td>-0.658±0.011</td>
<td>34.3±1.2</td>
<td>-146.6±9.7</td>
<td>-</td>
</tr>
<tr>
<td><strong>FATA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2×10⁻⁵</td>
<td>10.3±0.8</td>
<td>-0.619±0.008</td>
<td>176.6±10.2</td>
<td>-169.5±10.4</td>
<td>92.5±0.7</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>5.9±0.6</td>
<td>-0.624±0.007</td>
<td>191.6±10.8</td>
<td>-183.3±11.3</td>
<td>95.7±0.6</td>
</tr>
<tr>
<td>3.2×10⁻⁴</td>
<td>3.4±0.5</td>
<td>-0.607±0.008</td>
<td>177.2±8.4</td>
<td>-216.1±11.2</td>
<td>97.5±0.6</td>
</tr>
<tr>
<td>10⁻³</td>
<td>1.6±0.3</td>
<td>-0.645±0.004</td>
<td>185.4±8.9</td>
<td>-232.7±13.2</td>
<td>98.8±0.4</td>
</tr>
<tr>
<td>3.2×10⁻³</td>
<td>1.1±0.1</td>
<td>-0.621±0.003</td>
<td>194.7±8.6</td>
<td>-205.2±11.6</td>
<td>99.2±0.3</td>
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<tr>
<td><strong>FTDA</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3.2×10⁻⁵</td>
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</tr>
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<td>186.2±8.9</td>
<td>-192.4±7.4</td>
<td>97.0±0.4</td>
</tr>
<tr>
<td>3.2×10⁻⁴</td>
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</tr>
<tr>
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<td>-0.705±0.004</td>
<td>190.3±7.9</td>
<td>-221.2±11.2</td>
<td>98.6±0.1</td>
</tr>
</tbody>
</table>
high-frequency capacitive semicircle is associated with the interfacial charge-transfer reaction, the increasing inhibitor concentration could enhance the corrosion resistance of the steel. The low-frequency straight line is attributed to the diffusive Warburg impedance, which shows that the formed inhibitor film may affect the diffusion process of corrosive species. Furthermore, the impedance modulus (Z) over the whole frequency range in Bode plots increases continuously with the increasing inhibitor concentration. Two peaks are observed in the phase angle curves, indicating two time constants contained in the impedance spectroscopy. These results are consistent with the analysis of the impedance data present in the Nyquist diagrams.

The cutoff frequency, $f_c$, which is defined as the frequency at the maximum of the imaginary impedance in Nyquist diagram, can be used to estimate the corrosion activity of the steel because it is inversely proportional to the time constant ($\tau$) of a Randles circuit for corrosion processes. The values of $f_c$ for individual impedance plot are labeled in Figure 3. It is seen in Figure 4 that the cutoff frequency reduces continuously along with the increasing inhibitor concentration, indicating the enhanced corrosion resistance of the steel.

Figure 5 shows the equivalent circuits used to model and fit the impedance parameters for different systems. Particularly, ideal capacitors are replaced with constant phase elements (CPE), representing the non-ideal capacitive behavior for inhomogeneous electrodes. The impedance of the CPE is expressed by:

$$Z_{\text{CPE}} = Y_{\text{CPE}}^{-1} (j\omega)^{-n}$$

where $Y_{\text{CPE}}$ is the modulus ($\Omega^{1-n} \cdot \text{s}^{n} \cdot \text{cm}^{2}$), $\omega$ is angular frequency (rad/s), and exponent $n$ ($-1 \leq n \leq 1$) denotes the distribution of time constant. In the inhibitor-free solution, the Nyquist diagram contains two overlapped capacitive semicircles, which are associated with the
interface charge-transfer reaction in the high-frequency range and the coverage of corrosion scale such as FeCO₃ in the low-frequency range, respectively.²² The equivalent circuit in Figure 5(a) is used to fit the impedance parameters measured in the inhibitor-free solution, where $R_s$ is solution resistance, $CPE_{dl}$ and $R_{ct}$ are the constant phase element of double-charge layer and charge-transfer resistance, respectively, and $CPE_{ads}$ and $R_{ads}$ are the constant phase element and resistance of the adsorptive inhibitor, respectively.

When inhibitors are added in the solution, but at a low concentration of $3.2 \times 10^{-5}$ M, the impedance plots for FATA and FTDA are almost identical. Two distinctive segments can be identified where a linear relationship between log $Z$ vs. log $f$ with a slope close to −1 is present. Moreover, the phase angle approaches 90°. This indicates the formation of a compact, protective inhibitor film, whereas the diffusive impedance is in the lowest frequency range. The equivalent circuit in Figure 5(c) gives the best fitting to the impedance data.

The fitting electrochemical impedance parameters are shown in Table 3. The goodness of fit ($\chi^2$) in all cases is less than $10^{-3}$, indicating the suitability of the proposed equivalent circuits to fit the impedance data. In general, the two inhibitors greatly increase the $R_{ct}$ and $R_f$ values, which are further increased with the inhibitor concentration. The inhibition efficiency can be up to 97.5% at the inhibitor concentration of $3.2 \times 10^{-3}$ M in the solution. Meanwhile, the values of $C_{dl}$ and $C_f$ decrease as a result of the coverage of a film.

A quick comparison of the inhibition efficiencies calculated from the electrochemical polarization and EIS parameter, as shown in Tables 2 and 3, shows that the results are consistent each other. For the two inhibitors, the inhibition efficiency can be up to 98% when the inhibitor concentration is $3.2 \times 10^{-3}$ M. Thus, both polarization curve and EIS measurements are reliable to derive the inhibition efficiency.

### Scanning Electron Microscope Morphological Observation

Figure 6 shows the SEM surface morphology of X65 steel electrode after 24 h of immersion in the solution containing $3.2 \times 10^{-5}$ M and $10^{-3}$ M of FATA and FTDA inhibitors, respectively. At the low concentration of $3.2 \times 10^{-5}$ M, the surface of the electrode contains a film with cracks and a flaky structure, as seen in Figures 6(a) and (b). As the inhibitor concentration is up to $10^{-3}$ M, the films formed on the steel surface are much more compact and uniform, as shown in Figures 6(c) and (d). This gives direct evidence that an increasing inhibitor concentration in

<table>
<thead>
<tr>
<th>Inhibitor concentration (mol/L)</th>
<th>$R_{ct}$ (kΩ·cm²⁻¹)</th>
<th>$Y_{CPE_{dl}}$ (Ω⁻¹·cm²·s⁻ⁿ·10⁻⁶)</th>
<th>$n_{dl}$</th>
<th>$R_f$ (Ω·cm²)</th>
<th>$Y_{CPE_{f}}$ (Ω⁻¹·cm²·s⁻ⁿ·10⁻⁶)</th>
<th>$n_f$</th>
<th>$\eta_{eff}$%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Blank</strong></td>
<td>325.8±11.3 Ω·cm²</td>
<td>184.5±13.1 Ω⁻¹·cm²·s⁻ⁿ·10⁻⁶</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>FATA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3.2 \times 10^{-6}$</td>
<td>2.6±0.1</td>
<td>64.4±5.7</td>
<td>0.9</td>
<td>56.9±4.7</td>
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<td>0.84</td>
<td>87.5±0.9</td>
</tr>
<tr>
<td>$10^{-4}$</td>
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<td>57.6±5.4</td>
<td>0.8</td>
<td>267.3±13.2</td>
<td>30.9±4.1</td>
<td>1</td>
<td>91.4±0.7</td>
</tr>
<tr>
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<td>43.1±5.5</td>
<td>0.9</td>
<td>318.6±18.8</td>
<td>32.5±3.9</td>
<td>1</td>
<td>95.1±0.6</td>
</tr>
<tr>
<td>$10^{-3}$</td>
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<td>37.6±4.5</td>
<td>0.9</td>
<td>404.6±22.1</td>
<td>28.0±2.6</td>
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<td>$3.2 \times 10^{-3}$</td>
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<td>37.1±4.5</td>
<td>0.8</td>
<td>393.5±20.1</td>
<td>28.8±2.9</td>
<td>1</td>
<td>98.6±0.3</td>
</tr>
<tr>
<td><strong>FTDA</strong></td>
<td></td>
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<tr>
<td>$3.2 \times 10^{-6}$</td>
<td>3.2±0.1</td>
<td>59.8±5.1</td>
<td>0.9</td>
<td>66.2±4.5</td>
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<td>89.8±0.8</td>
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<td>0.9</td>
<td>416.7±19.2</td>
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<td>$10^{-3}$</td>
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<td>0.9</td>
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<td>39.2±3.9</td>
<td>0.9</td>
<td>441.5±21.5</td>
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<td>97.6±0.4</td>
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</table>
the solution favors the formation of a high-quality film on the steel surface for enhanced corrosion inhibition. The morphological features of the formed film show that, at low inhibitor concentrations, the film can be dominated by iron carbonate scale. However, at high concentrations, the adsorptive inhibitor film is dominant as the corrosion-generated ferrous ion content is not sufficient to form continuous iron carbonate scale.

Furthermore, for FATA inhibitor, the formed film is characteristic of a tightly arrayed antenna structure. Comparably, in the presence of FTDA, the film appears to be an orderly weaved polymerization network. The difference in film structure is probably a result of the different molecular orientations in the inhibitor molecule structures.

**Scanning Vibrating Electrode Technique Characterization**

Figures 7 and 8 show the SVET maps measured on X65 steel electrode after 24 h of immersion in the solution and after 2 h and 24 h of addition of $10^{-3}$ M FATA and FTDA in the solution, respectively. This test simulates the delayed addition of corrosion inhibitors in the fluid that has corroded the steel for a while. In the absence of inhibitors in the solution [Figures 7[a] and 8[a]], corrosion occurs on the steel electrode, as indicated by the locally large anodic current density (blue-colored). The primary cathodic reaction region is also identified, as colored in green.

Upon addition of inhibitors in the solution, the anodic current density reduces, as indicated by the reduced current density level (blue-colored). Meanwhile, the cathodic current density also decreases. Thus, the developed inhibitors can inhibit both anodic and cathodic reactions during steel corrosion. Moreover, with the increase of the immersion time, both anodic and cathodic current densities further decrease, indicating that the inhibitor film either thickens or improves its structure. Furthermore, both inhibitors preferentially inhibit the regions with large anodic and cathodic current densities. This phenomenon may be associated with an oriented adsorption of inhibitors on the steel surface, which will be further discussed in the following sections.

**Electrochemical Quartz Crystal Microbalance Measurements and Analysis**

The EQCM measurement was used to investigate if a selective or oriented adsorption of inhibitor molecules occurs on the steel surface. Two testing scenarios were designed for this purpose. One was to add inhibitors in the solution before the freshly prepared steel electrode, named “fresh electrode,” was immersed in the solution, and the other was to add inhibitors to the solution after the steel electrode was immersed for 1 h, named “corroded electrode.” Figure 9 shows the apparent mass variation ($\Delta m$), determined by EQCM measurements, of the fresh and corroded electrodes after 12 h of immersion in the solution containing $10^{-3}$ M FATA and FTDA, respectively. It is noted that...
the mass changes are relative values, rather than absolute values, in terms of the summation of mass changes in various processes, such as the growth of inhibitor film, adsorption-desorption of corrosion products, etc. However, the curves of Δm vs. time are monotonic and continuous, without apparent fluctuations. This indicates that the inhibitors contribute to formation of a continuous film on the steel surface, inhibiting corrosion of the steel.23–24

Furthermore, from the EQCM mass change results, both FATA and FTDA inhibitors show similar adsorption kinetics on the steel surface. For the fresh electrode, the mass increase of inhibitor film as a function of time fits a parabolic law in the first stage, and

FIGURE 7. SVET maps measured on X65 steel electrode after (a) 24 h of immersion in the solution, and after (b) 2 h and (c) 24 h of $10^{-3}$ M FATA addition in the solution, respectively.
then follows a logarithmic law in the second growth stage. However, a transition from linear to logarithmic growth is observed for the corroded electrode. Moreover, the mass gain resulting from the film growth on the fresh electrode is twice of that on corroded electrode for both inhibitors. Moreover, from the mass gains measured by EQCM, the fresh electrode possesses a faster weight increase resulting from the film growth than the corroded electrode.

After EQCM measurements, polarization curves were measured immediately on both electrodes, and the results are shown in Figure 10. It is noted that, in order to ensure controlled electrode surface conditions, each test was conducted on a newly prepared steel electrode carefully following the preparation and testing procedures. It is interesting to see that the results are opposite of the EQCM analysis. The inhibition efficiencies of both inhibitors are calculated from the

**FIGURE 8.** SVET maps measured on X65 steel electrode after (a) 24 h of immersion in the solution, and after (b) 2 h and (c) 24 h of $10^{-3}$ M FTDA addition in the solution, respectively.
corrosion current density \( (i_{\text{corr}}) \), and there is a smaller inhibition efficiency for the fresh electrode. An ex situ SEM morphological observation, as shown in Figure 11, indicates that the films formed on the corroded electrode surface possess a much more compact, needle-like pattern than those formed on the fresh electrode. According to authors’ previous studies, this dense structure consisting of a needle-like, nano-wall shape possesses an appreciable hydrophobic property to enhance the corrosion resistance of steels.

As mentioned, at high inhibitor concentrations, such as \( 10^{-3} \) M, in the solution, the formed film on the steel surface is dominated by the inhibitor film, as the corrosion-generated ferrous ion content is not sufficient to form continuous iron carbonate scale. On the freshly prepared electrode surface, the weight increase is faster because of film formation and growth.
while the weight increases more slowly on the corroded electrode because the electrode surface has already been covered with corrosion products. It is derived from Figure 9 that the weight increase rates for fresh and corroded electrodes in FATA-containing solutions are 0.061 μg/cm²/min and 0.035 μg/cm²/min, respectively. From the morphological characterization in Figure 11, the films formed at the inhibitor concentration of 10⁻³ M are not iron carbonate scale. Instead, the film is a complex containing both inhibitor film and the scale, as analyzed by XPS and reported in the following section. Morphologically, the film formed on corroded electrodes is more compact than that formed on the fresh electrode. Moreover, the inhibition efficiency is larger for the corroded steel electrode than the freshly prepared electrode. Thus, the added inhibitors tend to form the complex film by reactions between the inhibitor molecules and the corrosion scale. This film is more effective for corrosion inhibition than the adsorptive inhibitor film formed on fresh electrode surface.

X-Ray Photoelectron Spectroscopy Characterization and Analysis

In order to illustrate the chemical nature of the inhibitor adsorption on the steel and provide further evidence for the proposed inhibitor film formation and growth mechanism, the XPS was used to characterize the inhibitor films formed on X65 steel after 12 h of immersion in acetic acid-containing oilfield formation water saturated with CO₂ in the presence of 10⁻³ M FATA inhibitor.

The Fe2p spectra of two inhibited steel electrodes exhibit similar discrete peaks with EB around 711 eV (Fe₂p₃/2) and 724 eV (Fe₂p₁/2). The Fe₂p₃/2 curves can be deconvolved into three main peaks representing two chemical states.²⁷ The one at 710.3 eV, which is for ferrous species, is associated with FeCO₃. The other one around 711.8 eV assigned to ferric species is attributed to FeOOH. The last one at 714.5 eV is ascribed to satellites of ferric species.²⁷ In the authors’ previous study,¹⁵ the presence of 3,000 ppm acetic acid in the CO₂-saturated oilfield formation water would degrade the protective FeCO₃ layer because of the decreased solution pH. Instead, the FeCO₃ scale is found to form on the steel surface in the presence of FATA and FTDA inhibitors, which implies that the two inhibitors are capable of reducing the acid degradation to the scale. Furthermore, the peak of FeOOH is diminished by changing the θ from 5° to 90°, indicating that the topmost Fe(III) probably originates from the hydrolysis and oxidation of Fe(II).²⁸ It is thus assumed that the ferrous scale may combine with inhibitors to form an insoluble complex existing in the subsurface region of the steel.

For O₁s spectra, the profiles of the electrodes in solutions containing two inhibitors display almost identical characteristic bonds, which primarily originate from two segments. One is associated with iron oxide such as FeCO₃ and FeOOH in Fe₂p spectra, and the other is assigned to C=O (531.68 eV) and C-O in the furan ring (534.8 eV) of inhibitor molecules. It is noted

**FIGURE 12.** High-resolution XPS spectra obtained on X65 steel electrode surface after 12 h of immersion in acetic acid-containing oilfield formation water saturated with CO₂ in the presence of 10⁻³ M FATA inhibitor.
that the peak areas of iron oxide are relatively smaller, and decrease remarkably by reducing the analyzed depth. This phenomenon is a result of the fact that the inhibitor molecules are the key constituent of the interfacial layer and cover the underlayer of FeCO$_3$ species. Moreover, the peak related to furan ring shifts positively to the EB of 534.6 eV compared with pure inhibitor (533.2 eV).

The contrast of N1s, S2p, and C1s spectra measured at 5° and 90° is not sufficiently obvious, and is thus not shown herein. Further discussions refer to the spectra measured at \( \theta = 45^\circ \). The deconvolution of the N1s signal obtained in FATA-containing solution can be fitted into two chemically distinct components located at 402.3 eV and 403.5 eV, respectively. The first peak is generally assigned to the chemically coordinated N atoms in azole ring, amino group, and -NH in hydrazine groups. The second peak is consistent with the protonated N atoms as a result of a minority of physically bonded species, which lead to a positive polarization and therefore an increase of EB. Indeed, the molecular conformation of FATA can yield intermolecular hydrogen bonds between H atoms of amino group and electron pair of N atoms in another amino-triazole molecule. This dual-connecting behavior may cause the chemical and physical adsorptions simultaneously, which are absent for FTDA, however, because of the different structure of thiadiazole rings. It is

<table>
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<th>Components</th>
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<th>( \theta = 5^\circ )</th>
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<tr>
<td>Fe$_{2p3/2}$</td>
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<td>710.2 (47.3%)</td>
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<td>O$_{1s}$</td>
<td>530.21 (4.4%)</td>
<td>530.21 (4.4%)</td>
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<tr>
<td>N$_{1s}$</td>
<td>399.6</td>
<td>402.31 (80.1%)</td>
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<tr>
<td>S$_{2p}$</td>
<td>162.26 (60.8%)</td>
<td>162.26 (60.8%)</td>
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<tr>
<td>C$_{1s}$</td>
<td>284.85 (77.9%)</td>
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<table>
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<tr>
<th>Components</th>
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<th>( \theta = 5^\circ )</th>
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<td>711.75 (16.6%)</td>
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<tr>
<td>O$_{1s}$</td>
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<td>N$_{1s}$</td>
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<tr>
<td>S$_{2p}$</td>
<td>163.36 (43.5%)</td>
<td>163.36 (43.5%)</td>
</tr>
<tr>
<td>C$_{1s}$</td>
<td>286.25 (13.6%)</td>
<td>286.25 (13.6%)</td>
</tr>
</tbody>
</table>

FIGURE 13. High-resolution XPS spectra obtained on X65 steel electrode after 12 h of immersion in acetic acid-containing oilfield formation water saturated by CO$_2$ in the presence of $10^{-3}$ M FTDA inhibitor.
probable that multilayer adsorptions occur for FATA on steel surface.

S\text{2p} spectra show signals composed of S\text{2p}_{3/2} and S\text{2p}_{1/2} peaks that are separated by 1.2 eV, with an area intensity ratio of about 2, indicating the feature of the spin-orbit splitting. The S\text{2p} core level of pure FATA is resolved into two peaks, with E\text{B} at about 162.2 eV and 163.4 eV, representing exocyclic S atoms. Four peaks are identified for FTDA, with E\text{B} from 162.1 eV to 165.5 eV, representing exocyclic and endocyclic S atoms, as listed in Table 4. Peaks representing endocyclic S atoms are not identified by comparison with the pure inhibitors. It is assumed that S atoms in thiadiazole rings, rather than exocyclic S atoms, are probably involved in chemical bonding with steel because the spectra of both inhibitors and the film-deposited steel do not differ remarkably at the peaks for thiol moiety.

In C\text{1s} spectra, the first peak at about 284.6 eV corresponds to C-C and C=C in hexagonal rings, while the second peak at a higher E\text{B} of about 286.2 eV represents C-N, C=N, and C-S in pentagonal rings. The third peak appears distinctively for FATA in either pure inhibitor or the FATA film-deposited steel at E\text{B} of 288.1 eV, which is attributed to C=N\text{\#} resulting from the protonated aminotriazole group. By comparing the spectra obtained from pure inhibitors and the inhibitor-deposited steel electrodes, there is no substantial difference in the shape and position observed for the first peak, suggesting that the inhibitor adsorption through benzene ring does not occur. However, the second peak is less intense on the steel surface, indicative of involvement in chemical bonding.

CONCLUSIONS

The developed FATA and FTDA inhibitors are able to decrease the corroboration rate of X65 pipeline steel in CO\text{2}-saturated oilfield formation water containing acetic acid by over 100 times at a concentration of 3.2 \times 10^{-3} M, and the inhibition efficiency can exceed 98% for each inhibitor. The inhibitors are mixed-type ones, reducing both anodic and cathodic current densities at individual potential, compared to those measured in the inhibitor-free solution, while the corrosion potential remains essentially constant. There is good agreement between the inhibition efficiencies obtained from the polarization curve measurements and those from the EIS results.

The inhibition efficiency of each inhibitor increases with its concentration in solution. At inhibitor concentrations below 10^{-4} M, the film formed on the steel surface can be dominated by iron carbonate scale, which contains cracks and a flaky structure. At concentrations above 10^{-3} M, the adsorptive inhibitor film is compact and continuous. Corrosion inhibition is attributed to the formation, on the surface, of a film that consists of an insoluble complex containing inhibitor film and ferrous scale.

Although the freshly prepared steel surface is associated with a more rapid weight increase resulting from the film growth than the corroded steel electrode, the corrosion inhibition of the added inhibitor is more effective for the corroded electrodes. This is attributed to the formation of the complex film by reactions of the inhibitor molecules and the pre-formed corrosion scale, and this film is more effective than the adsorptive inhibitor film for corrosion inhibition.

ACKNOWLEDGMENTS

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REFERENCES