ABSTRACT: Potentiodynamic polarization and electrochemical impedance measurements were employed to investigate the effect of acetic acid on the anodic dissolution of carbon steel in a CO2−H2S solution. Both polarization and impedance results unveil that the dissolution rate of carbon steel first increases and then decreases with an increase in acetic acid concentration. At lower concentrations of acetic acid, the corrosion rate increases due to the increase in cathodic current density. While the decrease in corrosion rate at higher acetic acid concentrations is attributed to the decrease in the anodic current density. The reaction mechanism of carbon steel dissolution in the CO2−H2S−acetic acid medium is elucidated along with the retrieval of kinetic parameters using the impedance data acquired at different overpotentials for various concentrations of acetic acid (1, 50, and 500 ppm). Further field emission scanning electron microscopy (FESEM) images confirm that the pitting corrosion occurs on carbon steel surface at higher acetic acid concentrations.

1. INTRODUCTION
One of the major problems in oil and gas industries is CO2 corrosion of steel pipelines carrying production fluids. The CO2 corrosion and the various factors affecting it have been analyzed extensively and reported in the literature.1−4 During this corrosion reaction, FeCO3 is precipitated as a corrosion product,5,6 as shown below

$$\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^-$$
$$2\text{H}_2^+(aq) + 2e^- \rightarrow \text{H}_2(g)$$
$$\text{H}_2\text{CO}_3(aq) \rightarrow \text{H}_2^+(aq) + \text{HCO}_3^-(aq)$$
$$\text{HCO}_3^-(aq) \rightarrow \text{H}_2^+(aq) + \text{CO}_3^{2-}(aq)$$
$$\text{Fe}^{2+}(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{FeCO}_3(s)$$

(1)

Similarly, the CO2 corrosion of carbon steel in the presence of a sulfur solution (H2S) has also been studied.7−10 The studies showed that even a very small amount of H2S (0.003−1.2 kPa) accelerates the corrosion process.8,11−13 The dissolution mechanism of carbon steel in the presence of H2S is given below9,13,14

$$\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeHS}^+_\text{ad} + \text{H}^+ + 2e^-$$
$$\text{FeHS}^+_\text{ad} + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{S}$$
$$\text{FeHS}^+_\text{ad} + \text{OH}^- \rightarrow \text{FeS} + \text{H}_2\text{O}$$
$$\text{H}_2\text{S} + \text{Fe}^{2+} \rightarrow \text{FeS} + 2\text{H}^+$$

(2)

The major corrosion product is FeS along with FeCO3. Depending on the prevailing conditions (concentration of H2S, temperature, and pH), either of these corrosion products form a stable protective layer on the carbon steel or dissolving in the corrosive medium.7,8,10,12

The production fluids usually contain volatile fatty acids such as acetic acid, formic acid, propionic acid, etc. It is reported that even small amounts of acetic acid (180 ppm) can cause severe corrosion of steel pipelines.15−18 Hedges and Mcveigh investigated the effects of acetate on CO2 corrosion using a rotating electrode, where both acetic acid and iron acetate were used as a source of acetate ions.19 The results showed that the rate of corrosion is increased by both sources. It is also reported that acetic acid increases the corrosion rate via cathodic reactions without affecting the anodic reactions.20−23 Gulbrandsen studied the effect of acetic acid on carbon dioxide corrosion at 80 °C and reported that a protective FeCO3 film was formed at 80 °C in the presence of 100 ppm acetic acid.24

Although the corrosion of carbon steel in CO2−acetic acid solution has been reported, the combined effect of acetic acid−H2S−CO2 on carbon steel corrosion needs to be explored as only scarce information is available in the literature.16,22,25 In the present work, the effect of various concentrations of acetic acid (1−500 ppm) on carbon steel...
corrosion in a CO$_2$–H$_2$S solution is being investigated using various electrochemical techniques. In particular, the electrochemical impedance spectroscopy (EIS) technique is employed to understand the dissolution reactions of carbon steel in the aforementioned system along with other techniques such as field emission scanning electron microscopy (FESEM).

2. RESULTS AND DISCUSSION

2.1. Potentiodynamic Polarization Measurements.

After the open-circuit potential (OCP) value becomes stabilized within 5400 s, polarization measurements were carried out at various concentrations of acetic acid. The results obtained are shown in Figure 1. The corrosion potential ($E_{\text{corr}}$) and the corrosion current density ($I_{\text{corr}}$) values were estimated from these plots using the Nova software, and the values obtained are presented in Table 1. It can be seen from these results that the $E_{\text{corr}}$ values move toward a more positive potential with an increase in the acetic acid concentration. On the contrary, the $I_{\text{corr}}$ value increases first and then starts decreasing with an increase in the acetic acid concentration. The maximum $I_{\text{corr}}$ value is observed for the system containing 50 ppm acetic acid. Although the corrosion rate decreases at higher concentrations of acetic acid, the $I_{\text{corr}}$ value at 500 ppm ($2.4 \times 10^{-4}$ A cm$^{-2}$) is higher than that of the blank solution ($6.0 \times 10^{-5}$ A cm$^{-2}$). It indicates that the carbon steel surface is not completely passivated with a corrosion product layer even at higher concentrations of acetic acid. Another interesting feature is that the cathodic current density significantly increases with an increase in acetic acid concentration compared to anodic current density, especially at lower concentrations of acetic acid. However, at higher concentrations of acetic acid, the anodic current density is also significantly increased.

| acetic acid concentration (ppm) | $E_{\text{corr}}$ (V) | $I_{\text{corr}}$ (A cm$^{-2}$) |
|--------------------------------|----------------------|---------------------------------|
| 0                              | −0.68                | $6.0 \times 10^{-3}$            |
| 1                              | −0.65                | $1.3 \times 10^{-4}$            |
| 5                              | −0.64                | $1.9 \times 10^{-4}$            |
| 10                             | −0.62                | $2.3 \times 10^{-4}$            |
| 50                             | −0.61                | $4.3 \times 10^{-4}$            |
| 100                            | −0.58                | $3.0 \times 10^{-4}$            |
| 500                            | −0.53                | $2.4 \times 10^{-4}$            |

2.2. Electrochemical Impedance Spectroscopy Measurements at OCP.

To get more insight, EIS experiments were conducted at OCP values. Figure 2 shows the impedance patterns obtained for pure CO$_2$ and the CO$_2$–H$_2$S system, while Figure 3 shows the impedance patterns after the addition of various concentrations of acetic acid to the CO$_2$–H$_2$S system. It is evident that the total impedance decreases with an increase in acetic acid concentration till 50 ppm and that a further increase in acetic acid concentration to 100 and 500 ppm increases the total impedance. These results match the findings of polarization results. Two capacitance loops were observed at lower concentrations of acetic acid (0 and 1 ppm), while three time constants (capacitance–inductance–capacitance loops) were observed for the remaining concentrations. The change in impedance patterns shows that the presence of a significant amount of acetic acid in the CO$_2$–H$_2$S medium affects the interface reactions on the metal surface. The appearance of inductance and capacitance loops in the mid- to lower-frequency regime at higher acetic acid concentrations is more likely due to the accumulation of acetate ions at the metal–solution interface.

The impedance data are further validated with Kramers Kronig transform (KKT) using Nova software (not shown here) and then analyzing by electrical equivalent circuit (EEC) model fitting. The circuit shown in Figure 4a is used to fit the EIS data obtained for the CO$_2$–H$_2$S system containing 0 and 1 ppm of acetic acid. The best-fit EEC parameters are presented in Table 2. The % error between simulated and experimental data is <5% in all of the cases. In general, $Q_1$ represents the constant phase element (CPE). $Q_1$ and $Q_2$ are used to model the impedance data at higher frequencies and lower frequencies, respectively, for lower acetic acid concentrations. The solution resistance is
The impedance data acquired for the remaining systems are fitted using the circuit shown in Figure 4b. $Q_3$ is used to model the impedance data at higher frequencies for higher acetic acid concentrations. $L$ and $C$ correspond to inductance and capacitance. The resistors $R_3$, $R_2$, and $R_1$ are used to model the resistance associated with the capacitance loop at higher frequencies, inductance loop at midfrequencies, and capacitance loop at lower frequencies. The retrieved EEC parameters are given in Table 3. A similar circuit is reported in the literature to model the Ti-HF system.27 The maximum corrosion rate for the system containing 50 ppm acetic acid is well captured by this EEC circuit. CPE consists of two parameters, $Y_0$ and $n$, where $Y_0$ is the CPE parameter and has a unit of capacitance and $n_i$ is the exponent of CPE whose value may lie between 0 and 1 (3). $n_i = 1$ is considered as an ideal capacitor, and $n_i = 0$ is considered as a pure resistor

$$\text{CPE} = \frac{1}{Y_0(j\omega)^n_i} \quad (3)$$

where $j = \sqrt{-1}$ and $\omega$ is the frequency.

The $Y_0$ value first increases and then decreases when the acetic acid concentration increases from 5 to 500 ppm, while $R_3$ shows the opposite trend.

Similarly, $L$ and $R_2$ exhibit a minima at 50 ppm. The lower value of $Y_0$ along with a higher “$n_i$” value at higher concentrations of acetic acid indicates that the carbon steel surface is covered by a corrosion product layer without completely passivating the carbon steel surface. The patterns simulated from these circuits are presented in Figure 5.

2.3. Surface Morphology Analysis by Field Emission Scanning Electron Microscopy (FESEM). The surface morphologies of carbon steel treated with various corrosive solutions are given in Figure 6a–d. Uniform corrosion was observed when carbon steel was immersed in the blank solution (i.e., solution not containing acetic acid) as well as in solution containing 1 ppm acetic acid. The increase in corrosion rate with the addition of 1 ppm acetic acid to the blank solution as observed in electrochemical measurements is clearly evident from the FESEM images (Figure 6b). However, when the concentration of acetic acid is increased to 50 ppm, many pits were observed on the carbon steel surface. The number of pits observed on the carbon steel surface is significantly reduced at higher acetic acid concentrations. Thus, the maximum current density at 50 ppm concentration of acetic acid during electrochemical measurements mainly arises from the pitting corrosion.

2.4. EIS Measurements at Overpotentials. To further elucidate the anodic dissolution mechanism of carbon steel in the $\text{CO}_2-\text{H}_2\text{S}-\text{CH}_3\text{COOH}$ medium, three different acetic acid concentrations were chosen (1, 50, and 500 ppm). EIS measurements were performed for these systems at different overpotential values (0.05, 0.15, and 0.25 V with respect to OCP). Three loops (capacitance loop in the high-frequency regime followed by inductance and capacitance loops in the mid- to lower-frequency regime) were observed for all three systems. In general, electrical double layer along with faradic reactions occurring at the metal–solution interface is represented by the capacitance loop in the high-frequency regime, while the remaining loops observed in the mid- and lower-frequency regimes are attributed to both faradic and nonfaradic reactions.28 The patterns do not change with respect to overpotential values. The decrease in the total

| parameters | $\text{CO}_2$ | concentration of acetic acid (ppm) |
|------------|---------------|----------------------------------|
| $R_{\text{oil}}$ ($\Omega$ cm$^2$) | 21 | 19.6 | 22.2 |
| $Y_{\text{el}}$ ($\Omega^{-1}$ cm$^{-2}$ s$^n$) | $2.9 \times 10^{-4}$ | $1.3 \times 10^{-3}$ | $1.6 \times 10^{-3}$ |
| $n_1$ | 0.87 | 0.73 | 0.74 |
| $R_1$ ($\Omega$ cm$^2$) | 39.3 | 27.1 | 19 |
| $Y_{\text{el}}$ ($\Omega^{-1}$ cm$^{-2}$ s$^n$) | $3.3 \times 10^{-4}$ | $6.7 \times 10^{-3}$ | $1.7 \times 10^{-2}$ |
| $n_2$ | 0.84 | 0.86 | 0.64 |
| $R_2$ ($\Omega$ cm$^2$) | 261 | 115.7 | 42.8 |

represented by $R_{\text{oil}}$. The resistors $R_1$ and $R_2$ are used to model the impedance data for lower acetic acid concentrations and represent the charge-transfer resistance and faradic/nonfaradic resistance, respectively. Both $Q_1$ and $Q_2$ values increase, while $R_1$ and $R_2$ values decrease with the addition of 1 ppm acetic acid to the $\text{CO}_2-\text{H}_2\text{S}$ medium. Here, $Q_1$ and $Q_2$ (similarly $Q_2$ and $R_2$) are coupled as these circuit elements correspond to the same reaction step in the overall dissolution process and thus exhibiting the contrary behavior. The decrease in overall impedance confirms that the dissolution rate increases with the addition of acetic acid.

Figure 4. EEC used to fit EIS data at OCP for carbon steel (a) in the solution containing pure $\text{CO}_2$, $\text{CO}_2-\text{H}_2\text{S}$, and $\text{CO}_2-\text{H}_2\text{S}$-1 ppm acetic acid and (b) in the solution containing $\text{CO}_2-\text{H}_2\text{S}$ and acetic acid of various concentrations (5, 10, 50, 100, and 500 ppm).
impedance with an increase in the overpotential value is attributed to the nonpassivating surface of carbon steel. At 0.05 V, the observed total impedance is lowest for the system containing 50 ppm acetic acid. This mimics the behavior observed from the polarization measurements and EIS measurements performed at OCP. The impedance data are further investigated using the reaction mechanism analysis (RMA) modeling approach.

2.5. Reaction Mechanism Analysis. The reaction pathway of the anodic dissolution process could be retrieved from the EIS data via the reaction mechanism analysis approach.29 The dissolution mechanism of Fe in various corrosive media is investigated using the RMA approach.29–32 In the present work, the following multistep mechanism, which involves four intermediate adsorbate species, is proposed to describe the impedance patterns obtained from EIS measurements.

\[
\text{Fe} \overset{k_1}{\rightarrow} \text{Fe}^{2+}_{\text{ads}} + e^{-} \overset{k_{-1}}{\rightarrow} \text{Fe}^{3+}_{\text{ads}} + e^{-} \overset{k_i}{\rightarrow} \text{Fe}^{2+}_{\text{sol}}
\]

\[

where \( \text{Fe}^{2+}_{\text{ads}} \) and \( \text{Fe}^{3+}_{\text{ads}} \) represent species of different oxidation states (+1 and +2) adsorbed on the carbon steel surface, whose steady-state surface coverage values are given by \( \theta_1, \theta_2, \theta_3, \) and \( \theta_4, \) respectively. As the system contains CO\(_2\) as well as H\(_2\)S, the formation of both FeCO\(_3\) and FeS is thermodynamically feasible. Thus, two different species with the same oxidation state are considered in this model. Energy-dispersive spectroscopy (EDS) measurements also confirm the presence of sulfur, oxygen, and carbon species on the surface at all acetic acid concentrations (results are not shown here).

A similar approach is reported in the literature.27,28,32 It is also noted that the solubility of ferrous acetate is higher than that of other ferrous-based corrosion products; thus, one might not expect the presence of an acetate layer on the carbon steel surface. Here, \( \text{Fe}^{2+}_{\text{ads}} \) and \( \text{Fe}^{3+}_{\text{ads}} \) correspond to the sulfides of iron, and similarly, \( \text{Fe}^{+}_{\text{ads}} \) and \( \text{Fe}^{2+}_{\text{ads}} \) correspond to the carbonates/oxides of iron. As the formation of these species might occur via multisteps, the species with oxidation state +1 are also considered here as intermediate adsorbates. Although the mechanism without the incorporation of \( \text{Fe}^{2+}_{\text{ads}} \) and \( \text{Fe}^{3+}_{\text{ads}} \) was tested with acquired EIS data, the data simulated from the suggested mechanism match well with the EIS experimental data. Here, \( k_1 \) and \( k_6 \) correspond to the chemical dissolution steps of Fe in a given corrosive medium. The important steps involved in deriving the equations to simulate the impedance data for the given suggested mechanism are shown here. The assumptions and the detailed RMA approach are reported in various other research works.29–31

The rate constant \( k_i \) of a given electrochemical reaction as a function of overpotential \( \psi \) and potential independent parameters \( k_{i0} \) and \( b \) is given by the following equation

\[
k_i = k_{i0} e^{b \psi}
\]

where

\[
b_i = \frac{\alpha n F}{RT}
\]

Here, \( \alpha \) is the transfer coefficient whose values range from 0 to 1, \( n \) is the number of electrons transferred in an electrochemical step, and \( T, F, \) and \( R \) denote temperature, Faraday constant, and ideal gas constant, respectively. The value of “\( b \)” is considered to be positive for forward reactions and negative for backward reactions.

The mass balance equations for the four adsorbate species involved in the suggested mechanism are given below

\[
\frac{d\theta_1}{dt} = k_1(1 - \theta_1 - \theta_2 - \theta_3 - \theta_4) - k_{-1}\theta_1 + k_{-1}\theta_2
\]

\[
\frac{d\theta_2}{dt} = k_2(1 - \theta_2 - \theta_1 - \theta_3 - \theta_4) - k_{-2}\theta_2 + k_{-2}\theta_3
\]

\[
\frac{d\theta_3}{dt} = k_3\theta_1 - k_{-3}\theta_3 - k_{-3}\theta_4
\]

\[
\frac{d\theta_4}{dt} = k_4\theta_2 - k_{-4}\theta_4 - k_{-4}\theta_4
\]

where “\( \tau \)” denotes the total number of active sites available on the carbon steel surface per unit area and “\( i \)” denotes time. By employing steady-state conditions, the mass balance equations could be simplified as follows

\[
k_1(1 - \theta_{1s} - \theta_{2s} - \theta_{3s} - \theta_{4s}) = k_{-1}\theta_{1s} - k_{-1}^0\theta_{3s} + k_{-1}^0\theta_{4s}
\]

\[
k_2(1 - \theta_{1s} - \theta_{2s} - \theta_{3s} - \theta_{4s}) = k_{-2}\theta_{2s} - k_{-2}^0\theta_{3s} + k_{-2}^0\theta_{4s}
\]

\[
k_3\theta_{1s} = k_{-3}\theta_{3s} + k_{-3}\theta_{4s}
\]

Table 3. EEC Fitting Results of EIS Data Obtained at OCP for the CO\(_2\)–H\(_2\)S System Containing Various Concentrations of Acetic Acid

| parameters | 5 | 10 | 50 | 100 | 500 |
|------------|---|----|----|-----|-----|
| \( R_{oa}(\Omega \text{ cm}^2) \) | 16.8 | 15.7 | 11.92 | 12.1 | 20.1 |
| \( Y_{o1}(\Omega^{-1} \text{ cm}^2 \text{ s}^\theta) \) | \( 1.6 \times 10^{-3} \) | \( 1.7 \times 10^{-3} \) | \( 1.94 \times 10^{-3} \) | \( 1.4 \times 10^{-3} \) | \( 6.2 \times 10^{-4} \) |
| \( n_1 \) | 0.7 | 0.73 | 0.8 | 0.77 | 0.9 |
| \( R_1(\Omega \text{ cm}^2) \) | 50.8 | 39.3 | 21 | 24.4 | 32.4 |
| \( L_1(\text{H cm}^2) \) | 182.6 | 136.4 | 90.4 | 93 | 95.3 |
| \( R_2(\Omega \text{ cm}^2) \) | 243.3 | 220.2 | 100 | 136.5 | 195.7 |
| \( C (\text{F cm}^{-2}) \) | 7.1 | 6.95 | 2.1 | 2.4 | 3 |
| \( R_3(\Omega \text{ cm}^2) \) | 5.5 | 5.3 | 4 | 4.8 | 5.1 |
Solving these equations simultaneously will yield the expressions for steady-state surface coverage values for the adsorbed species, as shown in 15–18.

\[ k_3 \theta_{2ss} = k_{-4} \theta_{1ss} + k_3 \theta_{3ss} \]  
\[ \theta_{1ss} = \frac{\epsilon + \eta \gamma}{1 - \eta \delta} \]  
\[ \theta_{2ss} = \gamma + \delta \theta_{1ss} \]  
\[ \theta_{3ss} = \alpha \theta_{1ss} \]  
\[ \theta_{4ss} = \beta \theta_{2ss} \]  
\[ \alpha = \frac{k_3}{k_{-3} + k_3} \]  
\[ \beta = \frac{k_4}{k_{-4} + k_6} \]  
\[ \gamma = \frac{k_1}{k_1(1 + \beta)} \]  

**Figure 5.** Experimental and simulated impedance plots from EEC for (a) pure CO₂ system; (b) CO₂–H₂S; and CO₂–H₂S containing various concentrations of acetic acid: (c) 1 ppm, (d) 5 ppm, (e) 10 ppm, (f) 50 ppm, (g) 100 ppm, (h) 500 ppm.
Under unsteady-state and steady-state conditions, the current density ($J$) equation could be expressed as

$$J = nF(k_1(1 - \alpha_1 - \alpha_2 - \theta_1 - \theta_3) - k_2\beta_1 - k_3\beta_2 + k_4\beta_3)$$

(25)

$$J = nF(2(k_3\theta_{3ss} + k_4\theta_{4ss}))$$

(26)

Differentiating 25 with respect to potential will yield faradic impedance ($Z_F$) as shown below

$$\frac{dJ}{dV} = (Z_{F,m/s})^{-1}$$

$$= nF \left[ \frac{d(k_1 + k_2)}{dV} \frac{1}{1 - \theta_{1ss} - \theta_{2ss} - \theta_{3ss} - \theta_{4ss}} \right]$$

$$- (k_1 + k_2) \left\{ \frac{d\theta_1}{dV} + \frac{d\theta_2}{dV} + \frac{d\theta_3}{dV} + \frac{d\theta_4}{dV} \right\}$$

$$- \frac{dk_1}{dV}\theta_{1ss} - k_1\frac{d\theta_1}{dV} + \frac{dk_2}{dV}\theta_{2ss} - k_2\frac{d\theta_2}{dV}$$

$$- \frac{dk_3}{dV}\theta_{3ss} - k_3\frac{d\theta_3}{dV} + \frac{dk_4}{dV}\theta_{4ss} - k_4\frac{d\theta_4}{dV}$$

$$+ \frac{dk_1}{dV}\theta_{1ss} + k_1\frac{d\theta_1}{dV} - \frac{dk_2}{dV}\theta_{2ss} - k_2\frac{d\theta_2}{dV}$$

(27)

The equation is further rearranged to get charge-transfer resistance ($R_t$)

$$R_t^{-1} = R_t^{-1} - nF(k_1 + k_{1-} - k_3 + k_2) \frac{d\theta_1}{dV}$$

$$+ (k_1 + k_2 - k_4 - k_{2-}) \frac{d\theta_1}{dV} + (k_1 + k_{3-} + k_2) \frac{d\theta_4}{dV}$$

$$+ (k_1 + k_2 + k_{4-}) \frac{d\theta_4}{dV}$$

(28)

where

$$R_t^{-1} = nF(k_1b_1 + k_2b_2)(1 - \theta_{1ss} - \theta_{2ss} - \theta_{3ss} - \theta_{4ss})$$

$$- (k_2b_{1-} - k_3b_3)\theta_{1ss} - (k_4b_{2-} - k_4b_4)\theta_{2ss}$$

$$- k_2b_{3-}\theta_{3ss} - k_2b_{4-}\theta_{4ss}$$

(29)

Further, $\frac{d\theta}{dV}$ expressions are obtained from mass balance equations after expanding by Taylor series expansion without considering higher-order terms, as shown below

$$\frac{d\theta_1}{dV} = (E_1 - a - c)(B_2 - h) - (B_2 - d)(E_1 - e - g)$$

$$\frac{d\theta_2}{dV} = (E_2 - e - g) - (A_2 - f) \frac{d\theta_3}{dV}$$

(30)

$$\frac{d\theta_3}{dV} = \frac{E_3 - A_3 \frac{d\theta_3}{dV}}{C_3}$$

(31)

$$\frac{d\theta_4}{dV} = \frac{E_4 - B_4 \frac{d\theta_4}{dV}}{D_4}$$

(32)

Figure 6. FESEM images of carbon steel in (a) blank solution and at various concentrations of acetic acid in the CO2−H2S system: (b) 1 ppm, (c) 50 ppm, and (d) 500 ppm.
Table 4. Best-Fit RMA Parameters Extracted for Carbon Steel Dissolution in Different Systems

| parameter | values for various concentrations of acetic acid in CO₂–H₂S system | units |
|-----------|---------------------------------------------------------------|-------|
|           | 1 ppm | 50 ppm | 500 ppm | 1 ppm | 50 ppm | 500 ppm | 1 ppm | 50 ppm | 500 ppm |
| R<sub>sol</sub> | 18 | 20 | 19 | Ω cm<sup>2</sup> |
| k<sub>b</sub> | 2.6 × 10⁻⁶ | 1 × 10⁻⁶ | 1.5 × 10⁻⁶ | mol s⁻¹ cm⁻² |
| b<sub>1</sub> | 10 | 8 | 6.6 | V⁻¹ |
| k<sub><sup>b</sup>2</sub> | 1 × 10⁻¹⁰ | 1 × 10⁻¹² | 1 × 10⁻¹² | mol s⁻¹ cm⁻² |
| b<sub><sup>b</sup>2</sub> | −33 | 0 | 0 | V⁻¹ |
| k<sub>3</sub> | 1 × 10⁻⁵ | 1.5 × 10⁻⁷ | 1.5 × 10⁻⁷ | mol s⁻¹ cm⁻² |
| b<sub>3</sub> | 6 | 7.5 | 7.8 | V⁻¹ |
| k<sub>4</sub> | 1 × 10⁻¹² | 1 × 10⁻¹² | 1 × 10⁻¹² | mol s⁻¹ cm⁻² |
| b<sub>4</sub> | 0 | 0 | 0 | V⁻¹ |
| k<sub>5</sub> | 1.2 × 10⁻⁶ | 1 × 10⁻⁶ | 1 × 10⁻⁷ | mol s⁻¹ cm⁻² |
| b<sub>5</sub> | 9 | 38 | 31 | V⁻¹ |
| R<sub>s</sub> | 1 × 10⁻¹² | 1 × 10⁻¹² | 1 × 10⁻¹² | V⁻¹ |
| k<sub>7</sub> | 0 | 0 | 0 | V⁻¹ |
| k<sub>8</sub> | 6.5 × 10⁻⁷ | 9 × 10⁻⁹ | 9 × 10⁻⁴ | mol s⁻¹ cm⁻² |
| b<sub>8</sub> | 8 | 11 | 6 | V⁻¹ |
| k<sub>9</sub> | 1 × 10⁻¹² | 1 × 10⁻¹² | 1 × 10⁻¹² | V⁻¹ |
| b<sub>9</sub> | 0 | 0 | 0 | V⁻¹ |
| k<sub>10</sub> | 3.5 × 10⁻⁹ | 2 × 10⁻⁸ | 2 × 10⁻⁸ | mol s⁻¹ cm⁻² |
| b<sub>10</sub> | 15 | 18 | 15 | V⁻¹ |
| k<sub>11</sub> | 3.5 × 10⁻⁹ | 4.5 × 10⁻⁹ | 4 x 10⁻⁹ | mol s⁻¹ cm⁻² |
| b<sub>11</sub> | 30 | 78 | 8.2 | V⁻¹ |
| Y<sub>n</sub> at OCP + 0.05 V | 9.9 × 10⁻⁸ | 9.9 × 10⁻⁴ | 9.9 × 10⁻⁴ | Ω⁻¹ cm⁻² s⁻¹ |
| n<sub>2</sub> at OCP + 0.05 V | 0.9 | 0.91 | 0.91 | |
| Y<sub>n</sub> at OCP + 0.15 V | 9.9 × 10⁻⁸ | 9.9 × 10⁻⁴ | 9.9 × 10⁻⁴ | Ω⁻¹ cm⁻² s⁻¹ |
| n<sub>2</sub> at OCP + 0.15 V | 0.92 | 0.93 | 0.95 | |
| Y<sub>n</sub> at OCP + 0.25 V | 9.9 × 10⁻⁸ | 9.9 × 10⁻⁴ | 9.9 × 10⁻⁴ | Ω⁻¹ cm⁻² s⁻¹ |
| n<sub>2</sub> at OCP + 0.25 V | 0.95 | 0.97 | 0.98 | |
| t<sub>0</sub> | 1 × 10⁻⁷ | 1 × 10⁻⁷ | 1 × 10⁻⁷ | mol s⁻¹ |

The final expression for total impedance (Z<sub>t</sub>) is obtained by assuming the model shown in Figure 7 and is given below

\[
Z_{total} = R_{sol} + \frac{1}{(Z_{Ems/Rs})^i + Y_0(i\omega)^n)}
\]

where \( R_{sol} \) is the solution resistance, \( Y_0 \) is the parameter of constant phase element (CPE), and \( n \) is the exponent of CPE. The RMA parameters, which are shown in Table 4, are retrieved using an optimization technique called sequential quadratic programming (SQP). The code is written in MATLAB. The main objective function of the optimization is to reduce the residue between experimental and simulated impedance data, as shown below

\[
\text{residue} = \sum [\omega_R(Z_{RMS-observed} - Z_{RMS-expected})^2]
\]

\[
+ \omega_I(Z_{Ims-observed} - Z_{Ims-expected})^2]
\]

where \( \omega_R \) and \( \omega_I \) are the weighing functions which were taken as unity in the present simulations.

The simulated EIS patterns along with experimental data are shown in Figures 8–10. Although a quantitative difference is observed between the experimental and RMA simulated impedance data, the suggested mechanism encapsulates the experimental trends observed in the EIS data quite well. The observations of three loops (capacitance–inductance–capacitance) and maximum current at the 50 ppm concentration of acetic acid are reproduced in the simulated data with the suggested mechanistic reaction pathway.
Besides suggesting a mechanism from RMA, one could estimate the rate of dissolution of various steps and the surface coverage of various adsorbed species on the given surface. From the best-fit RMA parameters, it was clearly evident that the rate of all backward steps in the suggested reaction scheme is significantly low compared to the rate of forward reaction steps. Hence, one can neglect the backward reactions and consider only the forward reaction steps in explaining the observed EIS data. For all of the acetic acid concentrations, $k_1$ is higher than $k_2$ and $k_5$ is higher than $k_6$. This reveals that most of the dissolution occurs via the first step. Although two steps were considered, the dissolution via $k_5$ is more compared to that via $k_6$, as shown in Figure 11. It was estimated that 86% of the total dissolution occurs via the $k_5$ step when the solution contains 1 ppm acetic acid at all of the overpotentials. Similarly, for 50 ppm acetic acid solutions, ~88% of the total dissolution occurs via the $k_5$ step at any given overpotential. When the concentration of acetic acid increases to 500 ppm, it was observed that the dissolution via the $k_5$ step is significantly reduced to 74% at 0.25 V overpotential. These trends clearly predict that the anodic reaction rate is suppressed at higher concentrations of acetic acid (500 ppm), as observed in polarization measurements.

Similarly, the increase in current density at lower concentrations of acetic acid is mainly due to the increase in cathodic current density as the anodic dissolution rate does not increase significantly (86% at 1 ppm vs 88% at 50 ppm).

The surface coverage of four adsorbed species is plotted against overpotential, as shown in Figure 12. The surface coverages of both $\theta_{\text{iss}}$ and $\theta_{\text{sas}}$ are negligible. As the Fe species with the +1 oxidation state in general are thermodynamically unstable, they are quickly converted into species with the +2 oxidation state. The surface coverage of $\theta_{\text{iss}}$ decreases with overpotential, while the surface coverage of $\theta_{\text{sas}}$ increases with overpotential. Besides, the surface coverage of $\theta_{\text{sas}}$ is lower than the surface coverage of $\theta_{\text{iss}}$ at any given overpotential for all acetic acid concentrations. It is most likely due to the fact that the dissolution rate of Fe$^{2+}$ is higher compared to the dissolution rate of Fe$^{3+}$.

In summary, the corrosion rate of carbon steel in the CO$_2$–H$_2$S medium is increased with the addition of acetic acid but only at lower concentrations. It is more likely due to the increase in cathodic reaction rate, i.e., the addition of acetic acid increases the supply of hydrogen ions by dissociation reaction,$^{21}$ which further gets reduced. The anodic dissolution of carbon steel in the CO$_2$–H$_2$S medium is less likely to be disturbed by acetic acid. However, at very high concentrations of acetic acid, due to the supply of more hydrogen ions to the metal interface, the adsorption of H$_2$S species on carbon steel is significantly reduced, which results in a lower anodic dissolution rate. Thus, the corrosion rate is significantly reduced at higher acetic acid concentrations.

### 3. CONCLUSIONS

The addition of acetic acid to the CO$_2$–H$_2$S medium strongly affects the corrosion of carbon steel. Both potentiodynamic polarization and impedance measurements indicate that the corrosion rate first increases and then decreases as acetic acid
concentration increases with a maximum corrosion rate observed at 50 ppm. The increase in corrosion rate at lower concentrations of acetic acid is mainly due to the increase in cathodic current density, while the decrease in corrosion rate at higher concentrations of acetic acid is mainly due to the decrease in anodic current density. FESEM images reveal that carbon steel undergoes uniform corrosion at lower acetic acid concentrations, while pitting corrosion is observed when the acetic acid concentration reaches 50 ppm. The reaction mechanism analysis of impedance data suggests the following multistep mechanism with four intermediate adsorbates for carbon steel in the CO$_2$–H$_2$S–acetic acid medium

$$
\begin{align*}
Fe & \rightleftharpoons Fe_{ad}^+ + e^- \quad k_i \\
Fe_{ad}^+ + e^- & \rightleftharpoons Fe^{2+} \quad k_j \\
Fe^{2+} + e^- & \rightleftharpoons Fe_{sol}^{2+} \quad k_k
\end{align*}
$$

Further, the RMA parameters extracted from the simulation suggest that most of the dissolution occurs via the $k_5$ step.

Figure 9. Best-fit RMA and experimental EIS data for 50 ppm acetic acid in the CO$_2$–H$_2$S system at different overpotentials: (a) 0.05 V, (b) 0.15 V, and (c) 0.25 V.

Figure 10. Best-fit RMA and experimental EIS data for 500 ppm acetic acid in the CO$_2$–H$_2$S system at different overpotentials: (a) 0.05 V, (b) 0.15 V, and (c) 0.25 V.
4. EXPERIMENTAL SECTION

4.1. Materials. Carbon steel coupons [C: 0.22−0.26%; Si: 0.11−0.14%; Mn: 1.03−1.06%; P: 0.04% maximum; S: 0.03% maximum; Cr: 0.03% maximum; and rest Fe] were used in all of the experiments. The electrolyte solution was prepared by 3.5 wt % NaCl, 0.0006 M Na$_2$S$_2$O$_3$, which is equivalent to 1.1 kPa of H$_2$S$^{14}$ and acetic acid of various concentrations (1, 5, 10, 50, 100, and 500 ppm). The solution was continuously purged with CO$_2$ prior to the measurement as well as during measurement. Considering the safety aspects, Na$_2$S$_2$O$_3$ was being used instead of H$_2$S. All of the experiments were carried out at room temperature (25 ± 2 °C).

4.2. Electrochemical Measurements. Electrochemical experiments were performed using a standard three-electrode flat cell system connected to Potentiostat [Metrohm Autolab, PGSTAT 204]. An Ag/AgCl (3 M KCl)-type reference electrode was used, while a Pt rod was used as the counter electrode. Prior to testing, the carbon steel sample was first ground sequentially using emery sheets of grades 180, 320, 600, and 1000. The steel was then ground with emery sheets (1.0 and 0.3 μm). Then, the sample was rinsed properly with deionized water, dried, and immersed into the respective solution for 72 h. At the end of 72 h, the sample was taken out, washed, and dipped into nitric acid (69%) for few seconds to remove the corrosion products from the surface. Then, the sample was washed with water, dried, and examined via FESEM (Zeiss, Sigma). The corrosion products obtained on the carbon steel surface were also examined using energy-dispersive X-ray spectroscopy (EDS) technique (Zeiss, Sigma).

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Notes
The authors declare no competing financial interest.

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