Heterocyclic Corrosion Inhibitors for J55 Steel in a Sweet Corrosive Medium

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ABSTRACT: The inhibitory effect of two heterocyclic porphyrin compounds, specifically 5,10,15,20-tetrais(pentafluorophenyl)-21H,23H-porphyrin palladium(II) (PF-1) and 4,4′,4″-(porphyrin-5,10,15,20-tetrayl)tetrakis(benzoic acid) (PF-2), was studied in a sweet corrosion environment (3.5 wt % NaCl + CO2) on J55 steel by means of weight loss and electrochemical methods. Surface changes were studied using contact angle, scanning electrochemical microscopy (SECM), and atomic force microscopy (AFM) techniques. It was established that PF-2 showed the superlative inhibition efficiency of average of about 93% at 400 ppm concentration. The inductive behavior of the J55 steel surface in the presence of inhibitors was confirmed by SECM. The AFM further confirmed that the surface roughness was considerably decreased in the presence of porphyrins. The surface wettability of the steel was also investigated, and the results established the formation of a water-repellent layer on the surface when porphyrins are absorbed and layer became more hydrophobic with PF-2. Thermodynamics studies showed that the inhibition efficiencies of two compounds evaluated by all measurements follow the Langmuir adsorption isotherm.

INTRODUCTION

Oilfields in Sichuan and Xinjiang provinces in China use J55 steel as the casing pipe and are inserted in the wellbores. Use of J55 steel is very common owing to its cost effectiveness among other steels and they have a wide range of applications. J55 steel is moderately low grade steel manufactured by both seamless and electric welding procedure. Sweet corrosion due to the occurrence of carbon dioxide is a key concern to oilfields and gas fields. Crude oil in the reservoir is believed to contain carbon dioxide, hydrogen sulphide, and other impurities. The formation water which is injected back into the reservoir to increase the pressure and stability is another source of carbon dioxide and water in the reservoir. The quantification of carbon dioxide and water in the reservoir leads to the formation of a weak carbonic acid which can cause severe corrosion to steel. A series of experiments proved that, at a given pH, this acid causes higher corrosion problem than strong mineral acids, similar to hydrochloric acid (HCl) and sulfuric acid (H2SO4), which dissociate in water completely.2,3,5–7 The pitting corrosion formed along with the uniform corrosion due to the sweet corrosion (CO2 corrosion) is difficult to detect under the coatings. This predominant localized attack is common and considered to be most dangerous for pipeline and casing steel in oilfields.8–13 The protection of steel from the internal corrosion is difficult to monitor and that can lead to fearsome accidents, failures, and ecological catastrophe.3,14 Use of corrosion inhibitors can provide a suitable solution to the problem that act by modifying the sweet corrosive environment. Corrosion inhibitors are more pragmatic, and the nature or the potential of the steel is not hindered by their addition to the system.15–19 Oilfields indulge corrosion inhibitors frequently as they do not interrupt with the recovery, production, or transportation of oil and gas.

Molecular compounds, including heteroatoms such as nitrogen, sulfur, and oxygen in addition to aromatic rings or those containing π-electrons in multiple bonds in their structure having high electron density are typically effective corrosion inhibitors.20–26 These organic inhibitors operate on the plane by the virtue of adsorption and influenced by the type of the electrolyte, the nature and surface morphology of the metal, as well as their chemical structure.27,28 The porphyrin molecules are very rich in heteroatoms, π-electrons, and multiple bonds intact in their structure. The aromatic rings can easily bond with the metal surface and their bulky size can cover the active centers to form a protective layer.29 This is the motivation to use them as potential corrosion mitigators. In our previous study, we had applied the porphyrins as inhibitors on N80 steel and J55 steel in a neutral and sweet corrosion environment and found the remarkable results.30

RESULTS AND DISCUSSION

Weight Loss. A plot drawn between the inhibitor concentration and efficiency is shown in Figure 1. It can be
seen from the figure that the inhibition efficiency increases with increase in the inhibitor concentration for both 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin palladium(II) (PF-1) and 4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrakis(benzoic acid) (PF-2) inhibitors. The boost in effectiveness with the concentration can be accredited to the configuration of a defensive layer by PF-1 and PF-2 molecules adsorbing on the metal surface. It is also extracted from the figure that inhibition efficiency of PF-2 (93%) is more than that of PF-1 (85%).

**Electrochemical Impedance Spectroscopy (EIS) Measurements.** The Nyquist plot (Figure 2a), Bode plot (Figure 2b), and frequency-phase angle plot (Figure 2c) were obtained for J55 steel in 3.5% NaCl solution saturated with CO₂ and PF solution. A depressed semicircle can be seen in the Nyquist plot with a capacitive loop and an inductive loop below the real axis. The formation of this inductive loop may be ascribed to the frequency dispersion, inhomogeneities, or steel dissolution. The shape of the Nyquist curves does not change for different concentrations of PF-1 and PF-2 in saturated 3.5% NaCl solution, but the diameter becomes larger at higher concentrations of inhibitors. The increase in the diameter is due to the better corrosion resistance of the J55 steel which may be credited to the inhibitor molecules blocking the active centers on the surface. PF-2 shows a bigger diameter than PF-1, indicating better adsorption of the inhibitor molecules causing the shielding effect on the metal surface and protecting it from the corrosive solution.

**Figure 2d** shows an equivalent circuit used in the study consisting of charge transfer resistors (R<sub>ct</sub>), in series, with inductance (L), a resistor (R<sub>s</sub>) representing the solution resistance, and constant phase element (CPE) instead of capacitance to fit the curve precisely. The CPE (Z<sub>CPE</sub>) with respect to impedance can be explained by

\[
Z_{\text{CPE}} = R_s + \left[ \frac{R_{ct}}{1 + (2\pi f R_{ct} C_{dl})^n} \right]
\]

(1)

Or this may be shown as

\[
Z_{\text{CPE}} = Y^{-1} (j\omega)^{-n}
\]

(2)

where \(\omega\) is the angular frequency, \(n\) is a physical factor with an experiential constraint (0 \(\leq n \leq 1\)), and \(f\) is the frequency in Hz. A lower value \((n = 0.695)\) obtained for sweet 3.5% NaCl solution indicates surface inhomogeneity caused because of roughness or corrosion products on the metal surface. The
higher value of $n$ (0.816) in the presence of inhibitors exhibits reduction in surface inhomogeneity because of the formation of a shield on the active centers present on the metal surface.

The impedance constraints obtained after fitting the curves with the help of circuit are listed in Table 1. Charge transfer value increases with increase in the inhibitor concentration because of the increase in the width of the electrical double layer and decrease in the local dielectric constant. This phenomenon can be ascribed to the adsorption of inhibitor molecules on the metal surface, thereby jamming the active sites at the metal–solution interface.\(^\text{38,39}\) PF-2 shows better inhibition efficiency of 92% at 400 ppm with an $R_\text{ct}$ value of 1490 $\Omega$ cm\(^2\), whereas PF-1 was limited to 85% at 400 ppm with $R_\text{ct}$ value of 810 $\Omega$ cm\(^2\).

It can be observed from Figure 2b,c that the low frequency impedance modulus increases in the presence of inhibitors than that in saturated 3.5% NaCl solution and phase angle shifts toward higher frequencies in the presence of inhibitors. The slope values of the saturated 3.5% NaCl solution (0.491), PF-1 (0.692), and PF-2 inhibitor (0.784) is close to 1, as shown in Table 2. This exhibits that the adsorption of the inhibitors on the J55 steel surface mitigates the corrosion.\(^\text{40}\) The phase angle–frequency plot for sweet 3.5% NaCl solution shows the utmost peak at 32.7°, PF-1 shows the top peak at 56.7°, and PF-2 shows the highest peak at 71.3°. The maximum peak values tend to approach toward 90°, which is a characteristic capacitive behavior and inherited by good corrosion mitigators.\(^\text{31}\)

**Polarization Measurements.** Figure 3 reveals the Tafel plots for J55 steel in 3.5% NaCl solution at room temperature with and without PF-1 and PF-2 inhibitors. The calculated values of the corrosion current density ($I_\text{corr}$), corrosion potential ($E_\text{corr}$), cathodic/anodic Tafel slopes ($b_\alpha$, $b_\beta$), and inhibition efficiency ($n$) are shown in Table 3.\(^\text{39}\)

Table 3 shows the magnitude of $b_\alpha$ and $-b_\beta$, $E_\text{corr}$ and $I_\text{corr}$ values changed without following a definite trend. The cathodic and anodic slopes decreased and the $E_\text{corr}$ values shifted within 85 mV, suggesting that PF-1 and PF-2 belong to mixed-type inhibitors. The mixed inhibitor action is effective on hydrogen evolution and metal dissolution, simultaneously, without modifying the overall course mechanism by covering the dynamic sites.\(^\text{42}\) The decrease in $I_\text{corr}$ values from 0.98 mA cm\(^{-2}\) for saturated 3.5% NaCl solution to 0.14 mA cm\(^{-2}\) for PF-1 and 0.07 mA cm\(^{-2}\) for PF-2 shows increase in the corrosion resistance of the J55 steel because of the molecules of inhibitors getting adsorbed on the surface. The adsorption of the inhibitor molecules can take place through π-bonding/reterodonation covering the available active regions and thereby mitigating corrosion.\(^\text{43}\)

**Adsorption Behavior of the Inhibitor.** Validation of PF-1 and PF-2 molecules adsorbing on the metal surface and the interactions between metal–inhibitor at the interface was explained through adsorption isotherms. Surface coverage ($\theta$) is linked with the adsorbate in the bulk of electrolyte ($C_{\text{inh}}$) as in the subsequent equation.\(^\text{44}\)

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

(3)

where $K_{\text{ads}}$ is the equilibrium constant for the adsorption/desorption process. The equation can be rewritten as

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

(4)

Several adsorption isotherms were tried to fit the weight loss values to get a linear fit. However, adsorption of PF-1 and PF-2 molecules followed the Langmuir adsorption isotherm. A plot between $C_{\text{inh}}/\theta$ versus $C_{\text{inh}}$ (Figure 4) gave linear-fit plots of PF-1 and PF-2 molecules with the correlation coefficient ($R^2$) ranging 0.99966 for PF-1 and 0.99998 for PF-2. $K_{\text{ads}}$ can be interrelated to free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$ as\(^\text{45}\)

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln(55.5K_{\text{ads}})$$

(5)

where $R$ is the gas constant and the value 55.5 represents the concentration of water in solution expressed in mol L\(^{-1}\). The values of $K_{\text{ads}}$ and $\Delta G_{\text{ads}}^{\circ}$ for PF-1 and PF-2 inhibitors are given in Table 4. The higher values of $K_{\text{ads}}$ (14483 M\(^{-1}\)) for PF-1 and (37535 M\(^{-1}\)) for PF-2 represent high affinity for adsorption isotherm. The negative values $-33.6$ kJ mol\(^{-1}\) of $\Delta G_{\text{ads}}^{\circ}$ for PF-1 and $-36.0$ kJ mol\(^{-1}\) for PF-2 ensure the spontaneity of the adsorption process and stability of the adsorbed film over the
steel surface. The values lie between 20 and 40 kJ mol\(^{-1}\) that perhaps suggests that both physical and chemical adsorption would occur.

**Contact Angle.** The surface of the J55 steel acted hydrophilic in 3.5% NaCl solution as is evident by the value 14.7\(^{\circ}\), while an increase in the contact angle (87.9\(^{\circ}\)) for PF-1 and (102.3) for PF-2 was observed as is depicted in Figure 5. The increase in the contact angle with concentration can be attributed to the hydrophobic metal surface because of the presence of inhibitor film.\(^{47}\) As can be seen from Figure 5, the hydrophobic nature of the metal increases with increase in the inhibitor concentration as the bulky inhibitor molecules form a film and cover the entire surface.

**Scanning Electrochemical Microscopy (SECM).** SECM tests were performed in ac-amperometry mode to get the 3-D figures and color map images of the metal surface in 3.5% NaCl solution and inhibited solutions.\(^{48}\) To ensure a similar distance of the tip at the metal surface for all the samples, the probe approach test was done prior to each test. The x-axis and y-axis color map and 3-D images are shown in Figure 6a−h.\(^{49}\)

A variation in the color map images of x-axis and y-axis of sweet 3.5% NaCl, PF-1, and PF-2 solution was observed as shown in Figure 6a,c,e. The variation is related to the current as it changes with the vicinity of the tip at the metal surface. As can be observed from the color map of the PF-1 and PF-2 inhibitors, the surface color is less varied in comparison to the 3.5% NaCl solution. This suggests that the surface is uniform and smooth in the presence of PF-1 and PF-2 while it begins to form cracks leading to surface roughness.\(^{50-53}\) When the tip is brought near the metal surface in sweet 3.5% NaCl solution, an increase in current can be seen both on x-axis and y-axis as shown in Figure 6b. The increase in the current is due to the direct contact of tip with the metal surface without any protective barriers. Thus, oxygen/solution diffusion can take place easily at the metal surface giving rise to corrosion.\(^{51-53}\) In the presence of PF-1 and PF-2 inhibitors, the current was seen to decrease as the tip approaches the metal surface as shown in Figure 6d,f. This may be due to the adsorbed inhibitor film formed on the metal surface that blocks the oxygen/solution diffusion. The J55 steel surface behaves conducting in sweet 3.5% NaCl solution (higher current) whereas it remains insulating in the presence of PF-1 and PF-2 inhibitors (lower current).\(^{54}\)

**Atomic Force Microscopy (AFM).** To extract more lines of evidence for the changes in surface morphology exposed to 3.5% NaCl solution and inhibitor solutions, AFM images were analyzed. The three-dimensional AFM images of the steel surface in saturated 3.5% NaCl solution showed a corroded surface and the maximum peak of surface roughness reached up to 200 nm as shown in Figure 7a. This may be due to the absence of a protective film on the metal surface.\(^{30}\) In the presence of the PF-1 inhibitor, the surface appears more uniform and the peak of surface roughness decreases to 100 nm as shown in Figure 7b. The peak of surface roughness was further observed to be 5.1 nm for the PF-2 inhibitor as the surface remains flat and smooth as shown in Figure 7c. These results vindicate that PF-1 and PF-2 can serve as potential corrosion mitigators for J55 steel.\(^{55}\)

**Inhibition Mechanism.** Information on adsorption of the inhibitor molecules on the metal surface can help to elucidate the mitigation process in the sweet corrosive environment. Heteroatoms such as N, F, and O help PF-1 and PF-2...
Figure 6. continued
molecules to form bonds/complexes with the steel and protects from the attack of 3.5% NaCl solution saturated with CO₂. The conjugated bonds and aromatic rings containing unshared π-electrons also contribute in the complex formation between the metal and the inhibitor. The lone pair of electrons is donated to the vacant d-orbitals of the Fe atoms (chemical adsorption) and filled orbitals of Fe gives back electrons to inhibitor molecules via reterodonation (back-bonding) thus, forming a strong protection layer. The lone pair of electrons is donated to the vacant d-orbitals of the Fe atoms (chemical adsorption) and filled orbitals of Fe gives back electrons to inhibitor molecules via reterodonation (back-bonding) thus, forming a strong protection layer.56,67

Carbonic acid is produced as the water molecules present in 3.5% NaCl solution react with carbon dioxide passed in the solution. The formation of acid in the solution cause the steel surface to turn positively charged and also accounts for protonation of the inhibitor molecules as shown in Figure 8. At the start Cl⁻ ions from the solution may get adsorbed on the positively charged steel surface, and then, the protonated inhibitor interacts with the Cl⁻ and get adsorb through electrostatic interactions (physical adsorption), by forming a protective layer (FeCl⁻ inhibitor⁺ads).58,59,73

### CONCLUSIONS

From the result of the present study, PF-1 and PF-2 inhibits corrosion of J55 steel in a sweet corrosion environment. PF-2 shows a better inhibition efficiency of 95% from the weight loss.
test, 92% from impedance studies, and 93% from Tafel polarization measurements than PF-1 at 400 ppm concentration. Addition of the PF-2 inhibitor increased the $R_{ct}$ values from 119 to 1490 $\Omega \text{cm}^2$. PF-1 and PF-2 acted as mixed-type inhibitors and adsorbed on the steel surface both physically and chemically. Moreover, the negative values of $\Delta G_{ads}^{\circ}$ revealed the spontaneity of the adsorption process. The surface wettability test of the steel established the configuration of a water-repellant layer on the metal surface with PF-2 being most hydrophobic. Therefore, it can be inferred that the inhibition roles of PF-1 and PF-2 are through the adsorption at the metal/solution interface as disclosed by the SECM and AFM micrographs. The inhibition efficiency followed the order PF-2 > PF-1 for weight loss and electrochemical studies. All the results are in fine consistency with each other.

### EXPERIMENTAL SECTION

**Materials and Solutions.** J55 steel samples (wt %): C 0.24; Si 0.22; Mn 1.1; P 0.103; S 0.004; Cr 0.5; Ni 0.28; Mo 0.021; Cu 0.019; Fe balance were used for the weight loss and electrochemical study. The steel coupons were mechanically cut into 30 mm $\times$ 3 mm $\times$ 3 mm dimensions, mechanically abraded, and washed with double distilled water followed by ethyl alcohol, respectively, before every test. The 3.5% NaCl solution was prepared with doubled distilled water, saturated with CO$_2$ for 40 min at 6 MPa, and then sealed with epoxy resin. All the tests were done using this saturated solution of 3.5% NaCl. Figure 9 represents the molecular structure of the two different porphyrins used. These porphyrins (400 ppm each) were refluxed in 3.5% NaCl to prepare inhibitor solutions for tests.

**Methods.** *Weight Loss Measurements.* Five solutions of 25, 50, 100, 200, and 400 ppm for both the porphyrins were prepared for the weight loss studies. Sample preparation and experiments were done according to ASTM standards at room temperature for 3 h. The subsequent equation was used to calculate the corrosion rate ($C_R$).

$$C_R (\text{mm/y}) = \frac{87.6W}{atD}$$

where $W$ is the standard weight loss of J55 steel samples, $a$ is the total area of J55 steel samples, $t$ is the immersion time (in h), and $D$ is the density of J55 steel in $(\text{g cm}^{-3})$. The inhibition efficiency ($\eta$ %) was calculated with the help of the following equation.

$$\eta\% = \frac{C_R - C_R^{\text{inh}}}{C_R} \times 100$$

where $C_R$ represents the corrosion rate of 3.5% NaCl solution and $C_R^{\text{inh}}$ represents the corrosion rate in the presence of inhibitor, respectively.

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![Figure 8.](image1)

**Figure 8.** Mechanism of corrosion mitigation of J55 steel in the presence of (a) PF-1, (b) PF-2, and inhibitor in 3.5% NaCl solution saturated with CO$_2$.

![Figure 9.](image2)

**Figure 9.** Structure of (a) PF-1 and (b) PF-2 porphyrins.
Electrochemical Measurements. Electrochemical workstation of Autolab GSTAT302N including FRA software for EIS measurements and data fitting was used to perform impedance and polarization studies. A four-cell cell was used with J55 steel as the working electrode, a platinum electrode as an auxiliary electrode, and a saturated calomel electrode as the reference electrode, and CO$_2$ was passed in the solution and sealed later with epoxy resin. The tests were started after a steady value of corrosion potential ($E_{corr}$) was obtained. A potential of ±300 mV versus $E_{corr}$ at a scan rate of 1 mV s$^{-1}$ was applied to obtain the Tafel curves. EIS measurements were investigated in a frequency range from 100 to 0.00001 kHz with an amplitude of 10 mV peak to peak. The analysis of anodic and cathodic Tafel curves provided corrosion current densities ($I_{corr}$) and inhibition efficiency using the subsequent relationship.

$$\eta \% = \frac{I_{corr}^0 - I_{corr}^{inh}}{I_{corr}^0} \times 100$$

where $I_{corr}^0$ represents the corrosion current 3.5% NaCl solution and $I_{corr}^{inh}$ represents the corrosion current of inhibited solution. The charge transfer resistance ($R_{ct}$) values were obtained from the Nyquist plots and the inhibition efficiency was calculated using the following equation.

$$\eta \% = \frac{R_{ct}^{inh} - R_{ct}^0}{R_{ct}^0} \times 100$$

where $R_{ct}^{inh}$ and $R_{ct}^0$ are the charge transfer resistance in the presence and absence of an inhibitor, respectively.

Contact Angle Measurements. The steel samples were exposed to the 3.5% NaCl solution and the inhibited solutions of various concentrations of porphyrins. The sessile drop technique was performed using a DSA100 KRÜSS to record the contact angles on the metal surface. Prior to each test, the surface was cleaned to avoid dust and contaminants which can hinder the contact angle, and a baseline test was run to establish the same commencement parameters. All the tests were recorded three times to get accurate information about the surface.

Scanning Electrochemical Microscopy. SECM analysis was carried out to examine the electrochemical behavior and possible defects on the metal surface. The J55 steel sample was used as the working electrode and a platinum tip was used as the probe, while Ag/AgCl in saturated KCl was used as the reference and counter electrodes, respectively. Line scan measurements were performed using a CHI900C workstation with a tip approach of ~10 µm at the metal surface. Prior to tests, a probe approach was run to establish the same tip-metal distance for all metal samples.

Atomic Force Microscopy. The surface of the J55 steel exposed in 3.5% NaCl solution and inhibited solution was studied using an NT-MDT AFM instrument. The surface roughness of each sample was recorded using the instrument.

Notes
The authors declare no competing financial interest.

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