Research Article

Electrochemical Investigation on Adsorption of Fluconazole at Mild Steel/HCl Acid Interface as Corrosion Inhibitor

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The interfacial behavior of fluconazole on mild steel in 1 M HCl solution was studied by electrochemical methods, namely, polarization (Tafel Plot) and Electrochemical Impedance Spectroscopy (EIS). The surface morphology of mild steel in the presence and absence of fluconazole was studied by Atomic Force Microscopy (AFM). The results of the study showed that fluconazole reduced the corrosion rate in HCl acid solution by adsorbing on the surface of mild steel. Tafel results suggest that fluconazole behaves predominantly as an anodic inhibitor and shows greater inhibition efficiency (96%) at 0.30 mM. Thermodynamical parameters suggest that fluconazole is adsorbed on mild steel mainly by chemical mode. The EIS studies reveal the formation of a thin barrier film on mild steel surface. The AFM image of mild steel immersed in optimum concentration of fluconazole has confirmed the film formation on metal surface.

1. Introduction

Acid solutions are widely used in ore processing, fertilizer manufacturing, oil refining, waste water processing, chemical synthesis, and pickling and descaling processes [1–4]. Active metals such as mild steel, Zn, and Al are employed in industries for fabrication purposes due to their easy availability and low cost, where surfaces are rapidly damaged in the presence of acids [5]. Among the various methods to control the destruction of these active metals in acid solutions, the use of inhibitors is quite popular [6–8]. Organic compounds containing heteroatoms like P, S, N, and O have been explored as good corrosion inhibitors [9–11]. They adsorb on the metal surface in the acid solutions either physically or chemically thereby blocking the corrosion reaction. However, most of these inhibitors suffer from nonbiodegradability and some of them are also toxic to living beings. In modern scenario, development of novel biodegradable and less toxic corrosion inhibitors is gaining importance. Biologically active molecules like sulfadimidine, sulfamethoxazole, cefatrexyl, apart from other antibacterial, and antifungal drugs have been reported as good corrosion inhibitors [12–18].

In the present study, adsorption behavior of an antifungal drug, fluconazole (2-(2,4-difluorophenyl)-1,3-di(1H-1,2,4-triazol-1-yl)propan-2-ol), was evaluated for changes that occur in mild steel/HCl acid interface in view of the fact that fluconazole contains two triazole rings with active centers like N and aromatic π electrons, which can aid adsorption on mild steel surface minimizing the corrosion process in HCl medium.

Perusal of the literature shows that the adsorption behavior and kinetics of fluconazole were evaluated for Al in acid media [19, 20].

2. Experimental Details

2.1. Materials. Mild steel specimens of composition S—0.02–0.03%, P—0.3–0.8%, Mn—0.4–0.5%, C—0.1–0.2%, and the rest Fe with 1 cm² exposed surface were used for the entire electrochemical studies.

Fluconazole received from IPCA laboratories Ltd, Mumbai, as a gift sample was used for the studies. AR grade HCl acid and double-distilled water were used for the entire study. The structure of the studied compound is given in Figure 1.
2.2. Electrochemical Studies. All the electrochemical studies were carried out using CH Electrochemical analyzer model 760D with CHI 760D software. Conventional three-electrode system was used for polarization and EIS studies. In this setup, polished mild steel with 1 cm² exposed surface area was used as working electrode, platinum electrode as an auxiliary electrode, and saturated calomel electrode as reference electrode. All the three electrodes were kept immersed in 1 M HCl both in the absence and presence of five different concentrations, namely, 0.03 mM, 0.08 mM, 0.16 mM, 0.24 mM, and 0.30 mM of fluconazole. This setup was kept in room temperature for 30 min and then electrochemical measurements were carried out.

The open-circuit potential (OCP) versus time measurement was carried out for 60 secs. EIS measurements were carried out at corrosion potential ($E_{corr}$) by changing the a.c frequency ranging from 0.1 Hz to 10000 Hz at 5 mV of amplitude. Nyquist and Bode plots were obtained. From the Nyquist plots, charge transfer resistance ($R_{ct}$) and double-layer capacitance ($C_{dl}$) of mild steel in presence and absence of fluconazole in 1 M HCl were computed. The simulation studies were carried out using ZView software. The inhibition efficiency was calculated by using $R_{ct}$ as in

$$IE(\%) = \left( \frac{R_{ct(i)} - R_{ct(b)}}{R_{ct(i)}} \right) \times 100,$$

where $R_{ct(i)}$ is the charge transfer resistance of fluconazole-contained solution and $R_{ct(b)}$ is the charge transfer resistance of the blank HCl solution.

The Tafel polarization curves were obtained by changing the electrode potential from −150 mV to −750 mV at open-circuit potential with a scan rate of 0.5 mV s⁻¹. The linear Tafel segments of cathodic and anodic curves were extrapolated to corrosion potential to obtain the corrosion current densities ($i_{corr}$). The inhibition efficiency was evaluated by using $i_{corr}$ values as given in

$$IE(\%) = \left( \frac{i_{corr} - i_{corr(i)}}{i_{corr}} \right) \times 100,$$

where $i_{corr}$ is the corrosion current without fluconazole and $i_{corr(i)}$ is the corrosion current with fluconazole.

2.3. Surface Analysis. The AFM images of polished mild steel surface along with those immersed in 1 M HCl alone and 1 M HCl with 0.3 mM of fluconazole for 2 hours were scanned using Nano Surf Easy Scan 2 instrument at the range of 50 mm.

3. Results and Discussion

3.1. OCP Studies. The OCP versus time plots for mild steel in blank acid and with different concentrations of fluconazole are shown in Figure 2. From the figures, the OCP of 1 M HCl acid was found to be −0.4939 V. For an increase in concentration of inhibitor from 0.03 mM to 0.30 mM, the OCP was shifted towards noble direction from −0.4722 to −0.4644 V, indicating that fluconazole controls mainly anodic metal dissolution reaction [21].

3.2. EIS Studies. Nyquist and Bode plots of mild steel in 1 M HCl in the absence and presence of various concentrations of fluconazole are shown in Figures 3, 4, and 5. It is clear from these plots that the impedance of the mild steel substrate increases with the increase in the concentration of inhibitor in 1 M HCl. It is worth noting that the change in the concentration of fluconazole did not alter the profile of the impedance behavior suggesting similar mechanism for the corrosion inhibition of mild steel by fluconazole at various concentrations.

The Nyquist and Bode plots display a single high frequency capacitive loop and a time constant, namely, solution resistance ($R_s$) and charge transfer resistance ($R_{ct}$).

The corrosion process that occurs at the interface in fact has two steps. The first is the oxidation of the metal which is a charge transfer process and the second is the diffusion of the metallic ions from the metal surface to the solution which is a mass transfer process.

Shapes of the Nyquist plots show that the corrosion inhibition of fluconazole is only by charge transfer process.
The impedance behavior of mild steel with and without addition of flunoxazole can be explained by the simplest model, namely, Randles circuit which includes the charge transfer resistance ($R_{ct}$) parallel with constant phase element (CPE) in series with solution resistance ($R_s$) as represented in Figure 6. It can be noted from the Nyquist plots that the capacitive loops are depressed with center under the real axis even though they have a semicircular appearance. Deviations of this kind are often referred to as frequency dispersion [23] which is attributed to the irregularities and heterogeneities of the solid surface [24, 25]. The imperfect semicircular Nyquist plot can be explained by the nonideal behavior of the double layer.

The impedance ($Z$) of CPE is given by (3)

$$Z_{\text{CPE}} = \frac{1}{(i\omega)^nA},$$

where $A$ is the proportionality coefficient, $\omega$ is the maximum frequency, $i^2 = -1$ (imaginary number), and $n$ is the surface irregularity factor ($0 \leq n \leq 1$).

Equivalent circuit of this type has been previously used to model the mild steel/acid interface. The replacement of $C_{dl}$ with the $\text{CPE}_{dl}$ significantly improved the quality of the fit [26]. If the electrode surface is homogeneous (free from defects) and flat, the exponential value ($n$) becomes equal to 1 and the metal solution interface acts as a capacitor with regular surface, that is, when $n = 1$ $A = \text{capacitance}$.

The lower value of $n$ for 1 M HCl (0.86) indicated the surface inhomogeneity which resulted from roughening of metal surface due to corrosion. Upon addition of flunoxazole, the $n$ value increased from 0.86 to 0.90 (0.30 mM) indicating the reduction of surface defects due to adsorption of inhibitor at MS/acid solution interface [27].

The calculated impedance parameters are depicted in Table 1. Perusal of the table reveals that $R_{ct}$ values increased with the increase in the concentration of flunoxazole, which is due to the increased adsorption of the inhibitor at high concentration. Decrease of $\text{CPE}_{dl}$ may be caused by a reduction of local dielectric constant and/or by an increase in the thickness of the electrical double layer. These results very much suggest that flunoxazole acts by adsorption at the...
metal/solution interface [28, 29]. The addition of fluconazole decreases the CPE$_d$ values as a consequence to the replacement of water molecules by the inhibitor at the electrode surface.

3.3. Polarization Studies. Figure 7 depicts the cathodic and anodic polarization curves of mild steel in 1 M HCl at 303 K in the absence and presence of different concentrations of fluconazole and the potential versus current graphs are represented in Figure 8. The electrochemical parameters such as corrosion potential ($E_{\text{corr}}$), cathodic and anodic Tafel slopes ($b_c$ and $b_a$), corrosion current density ($i_{\text{corr}}$), and polarization resistance ($R_p$) were extracted from Figures 7 and 8 using CHI software and are shown in Table 2. From the results, it can be observed that the corrosion current decreases while increasing the concentration of fluconazole. The decrease of current density is due to the adsorption of inhibitor molecules on mild steel surface to retard the corrosion reaction of electrode with simultaneous replacement of electrolyte solutions at the interface [30]. Further, on increasing the inhibitor concentration, $E_{\text{corr}}$ values were shifted towards mainly positive side. This suggests that fluconazole behaves predominantly as an anodic inhibitor. The Tafel constants, namely, $b_a$ and $b_c$, decreased with the increasing of fluconazole concentration and $b_a$ was more deviated compared to $b_c$, showing that fluconazole controls mainly the anodic metal dissolution [31].

The polarization resistance ($R_p$) increases with the increase of concentration of the inhibitor as well. The increasing of polarization resistance is mainly due to the adsorption of fluconazole on mild steel surface. Further, polarization resistances derived from Tafel plots (DC studies) and obtained from complex plane plots (sum of the $R_s$ and $R_{ct}$) (AC studies) are in good agreement with each other ($R_p = R_s + R_{ct}$).

3.4. AFM Studies. AFM is a powerful tool to investigate the surface morphology and it is very useful to determine the film formation on metal surface in corrosion inhibition studies. The AFM images of polished mild steel, mild steel in 1 M HCl with and without presence of 0.30 mM fluconazole, are shown in Figures 9, 10, and 11. The AFM image of mild steel surface in HCl appears severely damaged than mild steel in HCl with 0.30 mM of fluconazole. Moreover, the average roughness of polished mild steel and mild steel in blank HCl solution was calculated to be 82 and 450 nm, respectively. With the addition of inhibitor, the average roughness was reduced to 208 nm, which suggested the film formation of the inhibitor over the mild steel surface [32].

3.5. Adsorption Isotherms. Most of the corrosion inhibitors prevent metal dissolution by adsorption process (Badr, 2009). The % IE of fluconazole was studied by Tafel and EIS methods which suggest that the surface coverage ($\theta = \text{IE}\% / 100$) increased with the increasing of inhibitor concentration. To describe the adsorption behavior of fluconazole, several
Table 1: Electrochemical impedance parameters of mild steel in 1 M HCl in the absence and presence of different concentrations of fluconazole as extracted from Nyquist plots.

<table>
<thead>
<tr>
<th>Concentration of inhibitor (mM)</th>
<th>$R_s$ $\Omega \text{cm}^2$</th>
<th>$R_{ct}$ $\Omega \text{cm}^2$</th>
<th>CPE$_{dl} \times 10^{-3}$ $\text{Fcm}^{-2}$</th>
<th>CPE$_p$ $(n)$</th>
<th>IE% using $R_{ct}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.2300</td>
<td>2.988</td>
<td>2.0683</td>
<td>0.80437</td>
<td>—</td>
</tr>
<tr>
<td>0.03</td>
<td>1.3960</td>
<td>10.7600</td>
<td>1.1944</td>
<td>0.8115</td>
<td>72.23</td>
</tr>
<tr>
<td>0.08</td>
<td>1.63</td>
<td>18.61</td>
<td>0.4375</td>
<td>0.8202</td>
<td>83.94</td>
</tr>
<tr>
<td>0.16</td>
<td>1.863</td>
<td>31.02</td>
<td>0.6146</td>
<td>0.8422</td>
<td>90.37</td>
</tr>
<tr>
<td>0.24</td>
<td>1.273</td>
<td>39.49</td>
<td>0.3113</td>
<td>0.8686</td>
<td>92.43</td>
</tr>
<tr>
<td>0.30</td>
<td>1.463</td>
<td>48.68</td>
<td>0.42846</td>
<td>0.8765</td>
<td>93.86</td>
</tr>
</tbody>
</table>

Table 2: Tafel polarization parameters for mild steel in 1 M HCl in the absence and presence of different concentrations of fluconazole.

<table>
<thead>
<tr>
<th>Concentration of inhibitor (mM)</th>
<th>$-b_a$ $\text{V dec}^{-1}$</th>
<th>$-b_c$ $\text{V dec}^{-1}$</th>
<th>$E_{corr}$ $\text{V}$</th>
<th>$i_{corr} \times 10^{-3}$ $(\text{A cm}^{-2})$</th>
<th>$R_p$ $\Omega /\text{cm}^2$</th>
<th>Average OCP (V)</th>
<th>IE% using $i_{corr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.1498</td>
<td>0.1596</td>
<td>−0.492</td>
<td>7.052</td>
<td>5</td>
<td>−0.4939</td>
<td>—</td>
</tr>
<tr>
<td>0.03</td>
<td>0.1043</td>
<td>0.1241</td>
<td>−0.474</td>
<td>1.575</td>
<td>16</td>
<td>−0.4722</td>
<td>77.66</td>
</tr>
<tr>
<td>0.08</td>
<td>0.0882</td>
<td>0.1164</td>
<td>−0.465</td>
<td>0.7353</td>
<td>30</td>
<td>−0.4712</td>
<td>89.57</td>
</tr>
<tr>
<td>0.16</td>
<td>0.1002</td>
<td>0.1109</td>
<td>−0.472</td>
<td>0.4803</td>
<td>48</td>
<td>−0.4735</td>
<td>93.19</td>
</tr>
<tr>
<td>0.24</td>
<td>0.0823</td>
<td>0.1067</td>
<td>−0.461</td>
<td>0.3096</td>
<td>65</td>
<td>−0.4633</td>
<td>95.61</td>
</tr>
<tr>
<td>0.30</td>
<td>0.0874</td>
<td>0.1029</td>
<td>−0.462</td>
<td>0.2595</td>
<td>79</td>
<td>−0.4644</td>
<td>96.32</td>
</tr>
</tbody>
</table>

Langmuir isotherm assumes the adsorption of organic molecules as a monolayer over the metallic surface without any interactions with other molecules adsorbed [34]. By using this isotherm, the free energy of adsorption ($\Delta G_{ads}$) was calculated by plotting $\ln C$ (M) versus $\ln \theta/(1 - \theta)$. The value of adsorption equilibrium constant is calculated from the intercept of the straight line obtained from Figures 12 and 13. As shown in the results (Table 3), negative sign of $\Delta G_{ads}$ indicates that the adsorption process of fluconazole over mild steel occurs spontaneously. The values of $\Delta G_{ads}$ calculated by Tafel and impedance methods are $-35.39$ and $-32.01$ kJ mol$^{-1}$, respectively. These values are at the interval of physical adsorption and chemical binding and indicate chemical adsorption of the inhibitor [35].

The adsorption process depends upon the size, orientation, shape, and electric charge of the inhibitor in addition to the charge on the metal surface [36]. The chemisorption involves electron sharing between metal surface and the inhibitor, whereas physisorption may occur due to the interaction between the charged metal surface and protonated inhibitor. Polarization studies reveal that fluconazole predominantly controls the anodic dissolution reaction. The chemisorptive bonds could be formed due to the sharing of electron pair between metal and unprotonated hetero atoms of fluconazole. Further, it is also possible that there could be an interaction between the electrons of $\pi$ orbitals of fluconazole with metal surface [37].

4. Conclusion

From the studies, the following are concluded.

(i) Fluconazole behaves good corrosion inhibitor for mild steel in HCl medium.
(ii) The results of polarization studies reveal that fluconazole acts as a predominantly anodic inhibitor and controls the metal dissolution.
(iii) The results of EIS studies confirm the formation of barrier layer by fluconazole on mild steel surface and further the charge transfer process controls the corrosion.
(iv) The AFM images as well as the values of average surface roughness support the formation of barrier film.

adsorption isotherms have been tested and the Langmuir kinetic thermodynamic model fits the experimental data well. The Langmuir isotherm is given by [33] the following:

$$\ln \frac{\theta}{1 - \theta} = \ln K + \ln C, \quad (4)$$

$$K = \frac{1}{55.5} \exp \left( \frac{-\Delta G_{ads}}{RT} \right), \quad (5)$$

where $\theta$-degree is the surface coverage, $C$ is the molar inhibitor concentration, and $K$ is the equilibrium constant of the adsorption process.

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Table 3: Thermodynamic parameters derived from Langmuir isotherm for adsorption of fluconazole on mild steel in 1 M HCl at 298 K.

<table>
<thead>
<tr>
<th>Method</th>
<th>Equilibrium constant $(K) \text{M}^{-1}$</th>
<th>$R^2$</th>
<th>Free energy of adsorption $(\Delta G_{ads}) \text{kJmol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel</td>
<td>28853.89</td>
<td>0.995</td>
<td>−35.39</td>
</tr>
<tr>
<td>EIS</td>
<td>7346.65</td>
<td>0.997</td>
<td>−32.01</td>
</tr>
</tbody>
</table>
The corrosion inhibition of fluconazole can be attributed mainly due to chemisorption at mild steel/HCl acid interface as supported by the results of isotherm studies.

Acknowledgments

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References


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