Effect of clozapine on inhibition of mild steel corrosion in 1.0 M HCl medium

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\textbf{A B S T R A C T}

In this work, an eco-friendly antipsychotic, namely clozapine (CZP) was used to investigate the mild steel (MS) corrosion inhibition process in 1.0 M HCl using weight loss (WL) measurements, potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS). The performance of the CZP on the corrosion inhibition of MS was also evidenced by scanning electron microscopy (SEM). Results show that the CZP is a good inhibitor and inhibition efficiency (IE) reach 96\% at an optimum concentration of 10^{-3} M. Potentiodynamic polarization curves showed that the CZP affects both cathodic and anodic current and may be classified as mixed type inhibitor in HCl medium. In addition, the IE increased with a rise in CZP concentration. While the adsorption of tested compound on MS surface was found to follow the Langmuir isotherm. Furthermore, the molecular dynamic (MD) simulations, radial distribution function (RDF), and quantum chemical parameters have been calculated and discussed in view of the results earlier reported.

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1. Introduction

Good mechanical properties, ease of availability and economic considerations have made MS one of the widely used industrial metals. In aggressive environments, especially in the presence of HCl solutions, the MS can easily corroded, so, the study of its corrosion inhibition become very important due to the great economic loss \cite{1}. The chlorhydric acid is one of the most produced acid solutions because of their importance in many industrial applications such as acid pickling and acid cleaning, which can produce an aggressive environment \cite{2}. In this environment as well as others aggressive mediums, the chemical compounds used as corrosion inhibitors is considered as one of the most used techniques to reduce the dissolution of the metal and consequently the rise of their cycle life. The effectiveness of these chemical compounds against metal dissolution lies on the ability of an inhibitor to adsorb on metal surface through active sites in their structure, such as, heteroatoms (N, O, P and S) as well as cycle rings, which can significantly minimize the metal dissolution \cite{3}. Recently, in addition to determine the inhibitive performance of an inhibitor, the research has been focused on the search of the compounds with non-toxicity or green inhibitors \cite{4}. Among them, the drugs-based corrosion inhibitors have been investigated in different aggressive environments \cite{5-11}. In this case, the CZP is considered as an eco-friendly compound with large applications in medicinal and pharmacy \cite{12-17}. The choice of the CZP is based on the presence of many sources of electrons such as nitrogen atoms and aromatic rings, which can be induced the greater adsorption of CZP on MS surface. Kumar et al. \cite{18}, and others \cite{19-22} have studied the corrosion inhibition of steels using synthesized benzo- diazepine and piperazine derivatives, but the use of an eco-friendly compound with a benzoiazepine and piperazine in their molecular structure can be a good solution in view of environmental considerations.

Recently, the quantum calculations were used to give additional insights and to well understand the electrochemical results and non-know properties of the adsorption process. In this case, many studies were carried out. Among them, N. Soltani et al. \cite{23} have studied the corrosion inhibition of MS in acidic environments using three pyrimidine-2-thione derivatives, PTH, PTM and PTMO by experimental and theoretical calculations. In addition, Oguzie et al. \cite{24} have applied DFT method, experimental and MD simulation to understand the adsorption behavior of \textit{Termesia tchabula} extracts, noted, TC on the steel surface. The DFT calculations of selected organic constituent’s reveals that the TC adsorbed through the heteroatoms and conjugate bond in their constituents, the MD results suggest that the TC constituents adsorbed in flat-lying orientation. Using combined experimental and quantum chemical studies, Kumar et al. \cite{18} also studied the adsorption characteristics of two benzoazepine derivatives, noted, BBD and BMBD to interpret the inhibition mechanism of steel corrosion in acid media (15\% HCl). The theoretical calculations of BBD and BMBD reveal that the HOMO densities responsible of the electron donating ability are
mainly occupied on the benzodiazepine ring, while the tendency of the molecules to accept electrons associated to LUMO densities become from benzene rings. On the other hand, Z. Zhang et al. [25] and Si-Wei Xie et al. [26] applied the RDF in their works as analyze of the MD simulation. Si-Wei Xie et al. [26] studied the mechanism of adsorption process of 3,5-dibromosalicylaldehyde Schiff’s base, noted, L1, L2 and L3. The researchers reported that the binding length of C–Fe, O–Fe, N–Fe, and S–Fe were ~3.5 Å, suggesting that L1, L2 and L3 adsorbed mainly through these atoms.

In the present work, the inhibition action of a CZP compound on the MS corrosion in 1.0 M HCl solution was assessed using PED, EIS, WL measurements and the examination of the metal surface by SEM. Molecular modelling, including, DMOPO and MD simulations were also employed to further understand the adsorption process of CZP and to search of the possible correlation between the IE% and the molecular structure of tested inhibitor.

2. Materials and methods

2.1. Electrochemical and weight loss measurement

The effects of CZP on the MS corrosion were investigated using electrochemical techniques (EIS and PDP), and gravimetric measurements in the concentration range of 5 × 10⁻⁵ M to 10⁻³ M at 303 K. The chemical composition of MS is: 0.370% C, 0.230% Si, 0.680% Mn, 0.016% S, 0.07% Cr, 0.011% Ti, 0.059% Ni, 0.099% Co, 0.160% Cu, and the remainder iron. The WL tests were performed in the immersion time of 12 h at 303 K. For electrochemical tests, the MS was immersed into the test solution for 30 min until a steady-state (open circuit) potential was obtained. EIS measurements were performed with a frequency range of 10 mHz to 100 kHz and amplitude of 5 mV with 10 points per decade. The polarization curves were recorded by polarization from −800 to −200 mV/SCE with a scan rate of 60 mV/s⁻¹. More details for experimental conditions can be obtained in published articles of R. Salghi [27, 28]. The inhibitor molecule used in this paper was purchased from Sigma–Aldrich and have the structure presented in Fig. 1, which used without any pre-treatment.

2.2. Molecular modeling detail

2.2.1. DMOPO method

In this study, E_{DMOPO} (the Highest Occupied Molecular Orbital energy), E_{LUMO} (the Lowest Unoccupied Molecular Orbital energy) and Fukui functions indices calculations were performed using reliable DMOPO method implemented in the high-performance software (Materials Studio version 6.0) [29, 30]. The GGA is the gradient–corrected functional method was used with a double numeric plus polarization (DNP) basis set and a Becke One Parameter (BOP) functional. The solvation effects (aqueous phase) was included in DMOPO calculations by COSMO [31] controls.

\[ E_{\text{adsorption}} = E_{\text{total}} - (E_{\text{surface-solution}} + E_{\text{inhibitor-solution}}) + E_{\text{solution}} \]  \hspace{1cm} (1)

\[ E_{\text{adsorption}} = -E_{\text{binding}} \]  \hspace{1cm} (2)

where \( E_{\text{total}} \) is the total energy of the entire system, \( E_{\text{surface-solution}} \) is the total energy of Fe (1 1 0) surface and solution without the CZP and \( E_{\text{inhibitor-solution}} \) is the total energy of CZP and solution; and \( E_{\text{solution}} \) is the total energy of the H₂O molecules.

2.3. SEM

The analysis of steel sample in the acidic solutions with and without the optimum concentration of CZP (10⁻³ M) was performed after 12 h of immersion in uninhibited and inhibited solution using SEM. SEM (Hitachi TM-1000) with an accelerating voltage of 15 kV was used for the experiments.

3. Results and discussion

3.1. Potentiodynamic polarization curves

Typical polarization potentiodynamic plots for MS in 1.0 M HCl medium and in the presence of CZP at 303 K are graphically presented in Fig. 2. Table 1 collected the parameters derived from PDP plots, while the values of \( IE_{\text{corr}} \) are calculated using Eq. (3).

\[ IE_{\text{corr}} = \frac{\text{Icorr}}{\text{Iorr}} \times 100 \]  \hspace{1cm} (3)

where \( \text{Icorr} \) and \( \text{Iorr} \) are the corrosion current densities in uninhibited and inhibited medium, respectively.

Analysis of the PDP curves indicates that the addition of CZP decreases both cathodic and anodic current densities with the rise in the CZP concentration. The presence of tested CZP in the aggressive medium causes change in the anodic and cathodic branches with no significant trend in the shift of \( IE_{\text{corr}} \) values in all tested concentrations, suggesting that the CZP, in general, behaves as mixed type inhibitor [28] with no change in the corrosion mechanism occurred due to the addition of the inhibitor [33]. By inspecting the results in Table 1, we note that the \( \text{Icorr} \) decreases monotonically when the content of CZP increases in solution. \( \text{Icorr} \) reaches a value of 24.5 µA/cm² at a concentration of 10⁻³ M of the inhibitor. This value of \( \text{Icorr} \) led to an IE% of about 95.6% and confirm that the CZP is a good inhibitor against the corrosion of MS in HCl medium. The values of the cathodic, \( \beta_c \), and anodic, \( \beta_a \), Tafel lines, show slight changes with the presence of CZP, these results

**Fig. 1.** Molecular structure of the CZP.
suggests that the surface blocking effect of the adsorbed CZP diminish the anodic and cathodic reactions [34].

3.2. Electrochemical impedance spectroscopy measurements EIS

The protective effectiveness of CZP on the MS corrosion in the aggressive medium (1.0 M HCl) was performed by means of EIS method at 303 K after 0.5 h of immersion. Fig. 3 represents the influence of CZP concentrations on Nyquist impedance spectra. In the EIS experiments, with presence and absence of CZP, only single semicircles are observed with depression at low frequency. This depression is often associated to the non-homogeneity and roughness of the MS surface [35]. A remarkable increase of the depressed semicircle diameter is observed with the presence of CZP. generally, the EIS plots, loop-like capacitive is mainly attributed to the charge transfer process, while the increase of semicircle diameter with a rise in CZP concentration is the result of the adsorption of the inhibitor on the MS surface [36]. The equivalent circuit model is shown in Fig. 4 was used to analyze the EIS experiments, the parameters are collected in Table 2, while the double layer capacitance \( C_{dl} \) values are calculated using the Eq. (4):

\[ C_{dl} = \frac{1}{Q} R_{ct}^{-1-n} \]  

(4)

where \( Q \) is the CPE constant and \( n \) is a coefficient that can be used as a measure of surface inhomogeneity [37]. The Eq. (5) was used to calculate the IE_{Rct}:

\[ IE_{Rct} = \frac{R_{ct} - R_{ct}^{c}}{R_{ct}} \times 100 \]  

(5)

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration (M)</th>
<th>(-\nu_{cor} ) (mV/SCE)</th>
<th>(-\beta_{a} ) (mV/sec)</th>
<th>( \beta_{c} ) (mV/sec)</th>
<th>( I_{cor} ) (µA/cm²)</th>
<th>IE_{Rct} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.0</td>
<td>486</td>
<td>162.0</td>
<td>132.2</td>
<td>564</td>
<td>-</td>
</tr>
<tr>
<td>CZP</td>
<td>5 x 10^{-5}</td>
<td>488</td>
<td>169.7</td>
<td>98.9</td>
<td>76.7</td>
<td>86.4</td>
</tr>
<tr>
<td></td>
<td>1 x 10^{-4}</td>
<td>490</td>
<td>181.4</td>
<td>125.5</td>
<td>55.4</td>
<td>90.2</td>
</tr>
<tr>
<td></td>
<td>5 x 10^{-4}</td>
<td>485</td>
<td>165.8</td>
<td>121.7</td>
<td>40.5</td>
<td>92.8</td>
</tr>
<tr>
<td></td>
<td>1 x 10^{-3}</td>
<td>487</td>
<td>167.2</td>
<td>97.4</td>
<td>24.5</td>
<td>95.6</td>
</tr>
</tbody>
</table>

3.3. Weight loss measurements and adsorption isotherm

3.3.1. Weight loss measurements

The WL method can rise the ability of an inhibitor to more adsorb in studied metal surface because of the long immersion time [27]. But the values of corrosion parameters by WL would obviously different in comparison with those obtained electrochemically because the influence of the experimental conditions. The WL tests were performed in 1.0 M HCl at 303 K with different concentrations of the CZP. The IE% and \( W_{cor} \) values obtained from the WL measurements of the MS for various concentrations of the CZP in studied medium at 303 K after 12 h of immersion are calculated and collected in Table 3. The IE_{cor} (%) and surface coverage \( \theta \) were determined by using the following Eqs.(6)–(7):

\[ IE_{cor} = \frac{W_{cor} - W_{cor}^{c}}{W_{cor}} \times 100 \]  

(6)

\[ \theta = 1 - \frac{W_{cor} - W_{cor}^{c}}{W_{cor}} \times \theta = \frac{IE\%}{100} \]  

(7)

Fig. 2. Potentiodynamic polarization curves of MS in 1.0 M HCl in the presence and absence of different concentrations of CZP at 303 K.
where $W_{corr}$ and $W_{corr}'$ are the corrosion rates of the MS due to the dissolution in studied aggressive medium without and with the studied range of the CZP concentrations, respectively. $\theta$ is the degree of surface coverage of the inhibitor. It can be seen from Table 3, that the CZP inhibits the corrosion of the MS and the IEC increases with increasing inhibitor concentration. The values of $IEC$ obtained in this section are little higher than those obtained by the electrochemical techniques which may be due to the length immersion time resulting strong and stable adsorption. The values of $IEC$ of CZP are also higher than those calculated by Siikinen et al. [19], which have studied the inhibiting properties of 1H-benzo[b][1,4]diazepine-2-4(3H,5H)-dione for MS corrosion. The presence of the phenyl and methylpiperezine improve the electron release power which produces high inhibition efficiency. The values of inhibition efficiency obtained in three techniques (EIS, PDP and WL) are in good agreement as presented in Fig. 5. It should be noted that no significant increase in the inhibition performance was obtained above optimum concentration (Fig. 5).

3.3.2. Adsorption isotherm

Basic information on the interaction between the CZP and the MS surface can be provided by adsorption isotherm. Considering the length of immersion time, the degree of surface coverage ($\theta$) for tested CZP was calculated from WL method [42]. The Langmuir model was found to be the best fit among various tested isotherms (Frumkin, Freundlich and Temkin) and consequently the good descriptor for adsorption of the CZP on the MS surface (Fig. 6) [28].

$$\frac{C_{coh}}{\theta} = \frac{1}{K_{ads}} + C_{coh}$$  \hfill (8)

where $K_{ads}$ is the equilibrium constant of the adsorption process, $C_{coh}$ is the concentration of the tested compound in the solution. The free energy of adsorption $\Delta G_{ads}$ was calculated using the values of $K_{ads}$ by the Eq. (9) [28]:

$$\Delta G_{ads} = -RT\ln(K_{ads} + C_{solvent})$$  \hfill (9)

where $C_{solvent}$ is the molar concentration of solvent (For H$_2$O is 55.5 mol L$^{-1}$). The large $K_{ads}$ value (Table 4) obtained in this study; indicate the strong interaction between the MS surface and adsorbing molecules of CZP, which support the better-obtained IEC [23]. While the negative values of the adsorption free energy $\Delta G_{ads}$ suggest that, the CZP molecule adsorb spontaneously onto the MS surface and the protective film is highly stable [23]. The calculated value of $\Delta G_{ads}$ is around -38.6 kJ/mol, which may indicate that the adsorption mechanism of CZP on MS is complex mixed type adsorption, neither typical chemisorption nor typical physisorption, but involving both interactions types with a remarkable predominance of chemical interactions [43].

![Fig. 3. Nyquist diagrams for the MS electrode in 1.0 M HCl containing different concentrations of the CZP at 303 K.](image)

![Fig. 4. The electrochemical equivalent circuit used to fit the impedance spectra.](image)

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration (M)</th>
<th>$R_{ct}$ ($\Omega \times cm^2$)</th>
<th>$\eta$</th>
<th>$Q \times 10^{-4}$ ($\Omega \times cm^2$)</th>
<th>$C_{oh}$ ($\mu F/cm^2$)</th>
<th>$R_{ct}$ ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.0</td>
<td>29.35</td>
<td>0.89</td>
<td>1.751</td>
<td>91.8</td>
<td>-</td>
</tr>
<tr>
<td>CZP</td>
<td>$5 \times 10^{-5}$</td>
<td>230.2</td>
<td>0.84</td>
<td>0.88901</td>
<td>41.8</td>
<td>87.2</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{-4}$</td>
<td>352.5</td>
<td>0.85</td>
<td>0.06018</td>
<td>30.7</td>
<td>91.6</td>
</tr>
<tr>
<td></td>
<td>$5 \times 10^{-4}$</td>
<td>521.2</td>
<td>0.83</td>
<td>0.35324</td>
<td>25.5</td>
<td>94.3</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{-3}$</td>
<td>780.8</td>
<td>0.83</td>
<td>0.33777</td>
<td>18.9</td>
<td>95.2</td>
</tr>
</tbody>
</table>

![Table 2. EIS parameters for corrosion of MS in acid medium at various concentrations of the CZP at 303 K.](table)
34. Molecular modeling

34.1. DMOF calculation

In order to understand the structural and electronic properties, which provide the effectiveness of our inhibitor against steel dissolution, the theoretical calculations were carried out using reliable density functional theory method offered by DMOF module implemented in Materials studio software with GGA functional at DNP/BOP basis set. The optimized molecular structure of CZP is presented in Fig. 7. Based on the frontier molecular orbital theory, the distribution of HOMO and LUMO orbitals is a critical tool to predict the reactivity and consequently the ability of tested compound to adsorb on the steel surface. Low LUMO energy ($E_{\text{LUMO}}$) related to the electrons accepting ability of molecules [24]. While the higher of $E_{\text{HOMO}}$ in present investigation implies that CZP has strong electrons tendency donating to d-orbitals of surface Fe atoms [24]. It's clearly observed from the Fig. 7 that the benzodiazepine ring, phenyl and part of piperezine are the main responsible for the donating and accepting electrons to (from) steel surface, this conclusion is based on the distribution of the HOMO (ability to donate) and LUMO (ability to accept) orbitals which is located almost in the entire molecular structure of the CZP. The calculated quantum chemical parameters such as; $E_{\text{HOMO}}, E_{\text{LUMO}}, \Delta E$ and $\Delta N$ are listed in Table 5. The electron affinity (EA) and Ionization potential (IP) are deduced from EHOMO and ELUMO by the Eqs. (10) and (11):

\[
\text{IP} = E_{\text{HOMO}}
\]

(10)

\[
\text{EA} = E_{\text{LUMO}}
\]

(11)

Fig. 6. Plots of the Langmuir adsorption isotherm of the CZP on the MS surface at 303 K.

$$\text{M"ulliken electronegativity (} \chi \text{) and Absolute hardness (} \eta \text{) can be approximated using [44,45]:}$$

$$\chi = \frac{\text{IP} + \text{EA}}{2}$$

(12)

$$\eta = \frac{\text{IP} - \text{EA}}{2}$$

(13)

The fraction of electrons ($\Delta N$) transferred can be evaluated by Pearson electronegativity scale:

$$\Delta N = \frac{Z}{(\eta_{\text{HOMO}} + \eta_{\text{LUMO}})}$$

(14)

where $Z$ is the work function of the iron surface with the value of 4.06 eV for Fe (1 1 0) [46,47]. $\chi_{\text{in}}, \text{is the absolute electronegativity associated to the inhibitor molecule, } \eta_{\text{HOMO}} \text{ and } \eta_{\text{LUMO}} \text{ are the absolute hardness of metal and the inhibitor molecule, respectively. The values of theoretical parameters such as } E_{\text{LUMO}} (\approx 4.602 \text{ eV) and } E_{\text{HOMO}} (\approx 1.872 \text{ eV) presented in Table 5 are in good correlation with the distribution of HOMO and LUMO orbitals. In the same way, the difference between LUMO and HOMO energies (}\Delta E_{\text{gap}}\text{) is considered as the essential descriptor of the reactivity of an inhibitor, the least } \Delta E (2.73 \text{ eV) value, can explain the good inhibition property of tested inhibitor [48].}$$

It has also reported that the $\Delta N$ value measures the ability of a chemical compound to transfer its electrons to metal if $\Delta N > 0$ and vice versa if $\Delta N < 0$ [49-50]. In this study, the positive value of $\Delta N = 0.301$ presented in Table 5, suggest the high capability of CZP to donate electrons to the MS surface.

In order to obtain additional information about the donor-acceptor interactions, the Fukui function (FF) calculations are one of the useful means for this purpose. The local reactivity indices also define the most reactive regions in a molecule. The FF are calculated using the following Eqs. (15)-(16) [51,52]:

\[
\int f^a_k = q_k(N + 1) - q_k(N)
\]

(15)

\[
\int f^b_k = q_k(N) - q_k(N - 1)
\]

(16)

Table 5 presents the adsorption parameters for the corrosion of MS in 1.0 M HCl at 303 K.

Table 3

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration (M)</th>
<th>$W_{\text{corr}}$ (mg/cm² × h)</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.0</td>
<td>11.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CZP</td>
<td>$5 \times 10^{-5}$</td>
<td>0.1338</td>
<td>88.21</td>
<td>0.882</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{-4}$</td>
<td>0.0932</td>
<td>91.78</td>
<td>0.917</td>
</tr>
<tr>
<td></td>
<td>$5 \times 10^{-4}$</td>
<td>0.0541</td>
<td>95.23</td>
<td>0.952</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{-3}$</td>
<td>0.0288</td>
<td>97.46</td>
<td>0.974</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Slope</th>
<th>$K_{\text{ad}}$ (M⁻¹)</th>
<th>$R^2$</th>
<th>$\Delta C_{\text{ads}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZP</td>
<td>1.02</td>
<td>125.383</td>
<td>0.9998</td>
<td>-38.6</td>
</tr>
</tbody>
</table>

Fig. 5. The plots of C vs. $I/\chi$ obtained by PDP, EIS and WL methods at tested and higher concentrations.
Table 5
The computed quantum chemical parameters for CZP compound.

<table>
<thead>
<tr>
<th>Quantum parameters</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$\Delta E_{\text{PDOS}}$ (eV)</th>
<th>$\Delta N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>-4.602</td>
<td>-1.872</td>
<td>2.73</td>
<td>0.301</td>
</tr>
</tbody>
</table>

with the maximum value of $f_i$. While the maximum value of $f_i$ indicate
that this center is preferred for the electrophilic attack [52,53]. In this
investigation, it can be seen in the Table 6 that the C (5), N (7) and C (10)
are the most susceptible centers for the nucleophilic attack, and the N
(2), N (7) and Cl (16) are the preferred sites for the electrophilic attack.
These atomic sites further strengthening the interaction of the CZP and
the surface of metal.

3.4.2. MD simulations and radial distribution function

The MD simulations were carried out to better understand the interaction
between the CZP and Fe (1 1 0) surface. The simulations were
performed in the system containing 500 water molecules and one mol-
ecule of the CZP. After 500,000 steps, the system reaches the equilibrium
which explains that both the temperature and energy reach a balance as
observed in the Fig. 8 [54]. By inspection of the Fig. 9, it could be ob-
served that the CZP adsorb nearly to Fe (1 1 0) surface, were a chemical
interactions can possibly occur through reactive sites in the molecule as
interpreted in experimental and theoretical study. In this case, the CZP
molecule protects the steel surface from the aggressive medium by
adsorbing on the Fe (1 1 0) surface in the possible nearly planar form,
reducing the MS dissolution [24,25]. The binding energy of the adsorp-
tion of CZP on Fe (1 1 0) is 1095.5 kJ/mol. The higher positive value of
binding energy suggests that the inhibitor adsorbs on the Fe (1 1 0) sur-
face easier, which can explain the high inhibitive performance of tested
CZP [55].

Other insights on the molecule-surface interaction modes can be
provided by structural analyze of the interactions with CZP and MS sur-
face simulated by the MD simulations. A RDF (or pair correlation func-
tion) $g(r)$ can be obtained after this analyze [25]. The RDF is used as a
useful method to estimate the bond length. The peak occurs at
1 Å – 3.5 Å, it’s an indication of small bond length, which correlated to
chemisorption, while the physical interactions are associated with the

Table 6
The Fukui indices of the CZP calculated using DMOF method.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$f^+$</th>
<th>$f^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (1)</td>
<td>0.023</td>
<td>0.049</td>
</tr>
<tr>
<td>N (2)</td>
<td>0.007</td>
<td>0.081</td>
</tr>
<tr>
<td>C (3)</td>
<td>0.041</td>
<td>0.010</td>
</tr>
<tr>
<td>C (4)</td>
<td>0.031</td>
<td>0.012</td>
</tr>
<tr>
<td>C (5)</td>
<td>0.099</td>
<td>0.046</td>
</tr>
<tr>
<td>C (6)</td>
<td>0.017</td>
<td>0.036</td>
</tr>
<tr>
<td>N (7)</td>
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<td>C (8)</td>
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<td>0.011</td>
</tr>
<tr>
<td>C (9)</td>
<td>0.022</td>
<td>0.025</td>
</tr>
<tr>
<td>C (10)</td>
<td>0.080</td>
<td>0.018</td>
</tr>
<tr>
<td>C (11)</td>
<td>0.028</td>
<td>0.027</td>
</tr>
<tr>
<td>C (12)</td>
<td>0.019</td>
<td>0.032</td>
</tr>
<tr>
<td>C (13)</td>
<td>0.049</td>
<td>0.057</td>
</tr>
<tr>
<td>C (14)</td>
<td>0.006</td>
<td>0.020</td>
</tr>
<tr>
<td>C (15)</td>
<td>0.036</td>
<td>0.042</td>
</tr>
<tr>
<td>Cl (16)</td>
<td>0.035</td>
<td>0.068</td>
</tr>
<tr>
<td>N (17)</td>
<td>0.014</td>
<td>0.033</td>
</tr>
<tr>
<td>C (18)</td>
<td>-0.012</td>
<td>-0.014</td>
</tr>
<tr>
<td>C (19)</td>
<td>-0.004</td>
<td>-0.004</td>
</tr>
<tr>
<td>N (20)</td>
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<td>0.001</td>
</tr>
<tr>
<td>C (21)</td>
<td>-0.001</td>
<td>-0.004</td>
</tr>
<tr>
<td>C (22)</td>
<td>-0.017</td>
<td>-0.012</td>
</tr>
<tr>
<td>C (23)</td>
<td>-0.003</td>
<td>-0.003</td>
</tr>
</tbody>
</table>

In the above equations, $q_i(N)$, $q_i(N + 1)$ and $q_i(N - 1)$ are the atomic
charges of the systems with N, N + 1 and N − 1 electrons, respective-
ly [53]. The atomic site prone to the nucleophilic attack is associated
peaks longer than 3.5 Å [25,26]. From the equilibrium configuration of CZP, the RDF of C, Cl and N atoms shows that the bonding length of Fe—N (3.42 Å), Fe—Cl (3.47 Å) and Fe—C (3.31 Å) are all less than 3.5 Å (Fig. 9). The results obtained confirm the highest ability of tested inhibitor to adsorb and consequently to protect the metal against dissolution, because of their highest capacity to donate and accept electrons to/from Fe metal through these active sites [26].

3.5. Scanning electron microscopy

The morphology of the steel surfaces in studied medium can be studied by SEM. In agreeing with the weight loss studies, the steel specimens were immersed in 1.0 M HCl solution for 12 h at 303 K in the absence and presence of optimum concentration (10^{-3} M) of the CZP; the specimens were dried and kept in a desiccator. The SEM images of steel immersed in 1.0 M HCl in the absence and presence of the optimum concentration of the CZP are shown in Fig. 10(a) and (b), respectively. The results of SEM reveal that the surface was damaged owing to corrosion in the absence of the inhibitor (blank), but in the presence of the inhibitor, in exception of some polishing lines, the surface of steel became smooth without any pits or cracks. These results are mainly associated to the good adsorption of CZP on the steel surface.

4. Conclusion

It can be concluded as follows:

1. Clozapine acts as good MS corrosion inhibitor in hydrochloric acid.
2. PDP measurements demonstrate that the CZP act as a mixed-type inhibitor.
3. In all tested experimental methods, the IEK increase with the rise in CZP concentration.
4. The adsorption of the CZP on the steel surface obeys the Langmuir adsorption isotherm. The adsorption occurs by chemical and physical interactions with predominance of chemical adsorption.
5. The results obtained from WL, PDP and EIS are in good agreement.
6. The molecular modelling including, DMO method and MD simulations support the good inhibitive performance of the CZP.
7. Surface morphological studied by SEM showed that a film of the CZP is formed on the steel electrode surface.


