Molecular Dynamics and Density Functional Theory Study on Corrosion Inhibitory Action of Three Substituted Pyrazine Derivatives on Steel Surface

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Abstract: A theoretical study for three derivatives of pyrazine namely 2-methylpyrazine (MP), 2-aminopyrazine (AP) and 2-amino-5-bromopyrazine (ABP), which are recently used as corrosion inhibitors for steel in 1.0 M H₂SO₄ medium, was undertaken by Density Functional Theory (DFT) at the B3LYP level. Their properties are most relevant to their potential action as corrosion inhibitor and have been calculated by $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, energy gap ($\Delta E$), dipole-moment ($\mu$), electronegativity ($\chi$), global hardness ($\eta$) and fraction of electron transferred from the inhibitor molecule to the metallic atom ($\Delta N$). To explain their inhibition performance, local reactivity of the molecule has been analyzed through Fukui function. Furthermore, the binding energies of the inhibitors with the Fe (0 0 1) surface are studied using Molecular Dynamics (MD) simulation method. The theoretical results are in well accordance with the recently reported experimental outcomes.

Keywords: Steel; Pyrazine Derivatives; Density Functional Theory Calculations; Molecular Dynamics Simulation

1. INTRODUCTION

Corrosion inhibitors are widely used in acid solutions for protection of metal surfaces from corrosion. Several organic compounds with hetero atoms like O, N, S, P and having multiple bonds are
useful and are widely used as effective corrosion inhibitors [1-5]. In different acid solutions the corrosion inhibition of metals generally depends on how the metals are interacting with the concerned organic molecule [6]. The organic molecules should have centres which are capable of forming coordination bonds with metal surfaces [7,8]. Stronger is the coordination bond, better is the inhibition efficiency. Their effectiveness as promising inhibitors is related to spatial molecular structural distribution, molecular electronic structure, chemical composition, surface charge density and of course to their affinity to the individual metal surface [9-11].

Pyrazine is a heterocyclic organic compound. This and its derivatives are useful inhibitor molecules in acid medium [12]. Pyrazines and its different substituted derivative e.g.; bromo, methyl and amino etc. have different inhibition efficiency depending on the availability of lone pair of electrons on hetero atoms and also based on metal-heteroatom interactions of concerned metal in acid solutions. Though the effectiveness of three pyrazine derivatives (e.g.; 2-methylpyrazine, 2-aminopyrazine and 2-amino-5-bromopyrazine) as corrosion inhibitors for steel in specific acid media have been reported in recent times [13], their mechanistic explanations based on quantum chemical studies are scanty in literature.

In this present paper quantum chemical calculation and molecular dynamics simulations have been performed to investigate the reaction mechanism of corrosion inhibition behaviour of pyrazine and its derivatives. It strengthen the fact that this type of calculation are proving to be a very important and cost effective tool for corrosion inhibition mechanism even without doing each and every wet chemical studies [14,15]. In recent times, with the massive advancement of computational hardwares, DFT and MD simulations have emerged as an attractive tool to the scientific community for predicting structural behaviour and reaction mechanism of several chemical species. By using this sophisticated computational method we can easily predict the systematic way for the analysis of the inhibitor/surface interaction. The inhibitor properties of different pyrazine derivatives have been reported in a recent experimental study. They proposed the inhibition efficiency increase in the order 2-methylpyrazine (MP) < 2-aminopyrazine (AP) < 2-amino-5-bromopyrazine (ABP) [13].

The very aim of this particular work is to extend this investigation to ascertain whether the experimentally predicted orders are fully supported by theoretical predictions by finding a clear relationship between calculated quantum chemical parameters and the experimentally determined inhibition efficiency of inhibitors. This is achieved by calculating relevant molecular properties of inhibitors and there by explaining the mechanism of inhibition of the inhibitors with the steel surface. The relative inhibition efficiency was calculated by quantum chemical indices: $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, energy gap ($\Delta E$), dipolemoment ($\mu$), electronegativity ($\chi$), global hardness ($\eta$) and the fraction of electrons transferred from the inhibitor molecule to the metallic atom ($\Delta N$) surface. Interaction of inhibitor molecules with Fe (0 0 1) surface using the molecular dynamics simulations was also investigated.

2. METHODOLOGY
2.1 Computational Details for Quantum Chemical Calculation

DFT calculations are performed in this present study with the ORCA programme (version 2.7.0) [16]. This is an open source code developed by Prof. Dr. Franc Neese (Director, MPI für Chemische Energiekonversion, Muelheim, Germany). Geometry optimizations of all inhibitor materials are performed with B3LYP [17-20] functional level of DFT. Ahlrichs group developed the all-electron Gaussian basis sets [21]. For carbon and hydrogens like atoms, slightly smaller polarized split-valence SV(P) basis sets are used which were double-ζ quality in the valence region and have polarizing set of d functions on atoms other than hydrogens. Here in triple-ζ quality basis sets TZV(P) with one set of
Figure 1. DFT-derived (a) Geometry optimized structure, Frontier molecular orbital density distribution: (b) HOMO and (c) LUMO plot of MP ligand.

Figure 2. DFT-derived (a) Geometry optimized structure, Frontier molecular orbital density distribution: (b) HOMO and (c) LUMO plot of AP ligand.

Figure 3. DFT-derived (a) Geometry optimized structure, Frontier molecular orbital density distribution: (b) HOMO and (c) LUMO plot of ABP ligand.
polarization functions on the atoms like N, Cl, Br etc. are hereby used [22]. SCF calculations are converged tightly (1×10⁻⁸ Eh in energy, 1×10⁻⁷ Eh in the density and 1×10⁻⁷ in maximum element of the DIIS error vector). Theoretical parameters are calculated in the liquid phase because electrochemical corrosion always happens in liquid phase. Therefore, it was necessary to include the effect of a solvent in the computational outcomes. This method model the solvent as a continuum of uniform dielectric constant (ε) where solute is placed as a uniform series of inlocking atomic spheres.

The local reactivity has been analyzed by evaluating Fukui indices (FI). The FI calculation are performed using Dmol³ module, Material studio™ version 6.1 by Accelrys Inc, San Diego, CA. All the calculation are performed using B3LYP exchange correlation functional and the double numeric with polarization (DNP) basis set, because this set is the best set available in Dmol³ [23]. Fukui indices are used to obtain the detail information of local reactivity [24]. The Fukui function \( f_k \) is defined as the first derivative of the electronic density \( \rho(\vec{r}) \) with respect to the number of electrons \( N \) in a constant external potential \( \nu(\vec{r}) \) [25].

\[
f_k = \left( \frac{\partial \rho(\vec{r})}{\partial N} \right)_{\nu(\vec{r})}
\]

The Fukui functions can be written by taking the finite difference approximations as [26]:

\[
f_k^+ = q_k(N + 1) - q_k(N) \quad \text{(for nucleophilic attack)}
\]

\[
f_k^- = q_k(N) - q_k(N - 1) \quad \text{(for electrophilic attack)}
\]

where \( q_k \) is the gross charge of k atom i.e; the electronic density at a point \( r \) in space around the molecule. The \( q_k(N+1), q_k(N) \) and \( q_k(N-1) \) are defined as the charge of the anionic, neutral and cationic species respectively. Here Fukui function are obtained through the finite difference approximation using Hirschfeld population analysis (HPA) [27].

2.2 Computational Details for Molecular Dynamics Simulation

Adsorption behaviour of inhibitor molecule is very much important to understand the corrosion behaviour on metal surface. Molecular dynamics (MD) simulation is the technique, which has become popular towards finding the preferential adsorption sites on metal surfaces. The interaction between Fe (0 0 1) surface and inhibitor molecules is carried out in a simulation box (37.26 × 37.26 × 77.23 Å) with periodic boundary conditions. Material studio™ 6.1 [28] by Accelrys Inc. has been used to build Fe (0 0 1) surface and inhibitor molecules. A vacuum slab of 50 Å heights is kept on the Fe (0 0 1) surface. The number of layers is chosen in such a way that depth of the surface is greater than the non bond cut-off radius used in this calculation. Ten layers of iron atoms provide sufficient depth to overcome the issues related to cut-off radius in this case. After constructing the initial geometry of the surface and inhibitor molecules, geometry optimization is done in order to get rid of the unfavourable structures and minimize the energy of the initial geometries. The iron substrate with (0 0 1) plane was first optimized to the minimum energy. Then inhibitor molecule is placed near to the Fe (0 0 1) surface plane. The behaviour of the inhibitors molecules on the Fe (0 0 1) surface was then simulated by Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. COMPASS is an ab initio force field. Most parameters were derived based on ab initio data. In general, the parameterization procedure can be divided into two phases: ab initio parameterization and empirical optimization [29]. The MD simulation was performed under canonical ensemble (NVT) at a temperature of 298K using a time step of 1.0 femto second. In each case, simulation is performed upto 50 ps. The interaction energy as well as binding energy between the inhibitor molecules and Fe (0 0 1) surface was calculated using Equation 1.
and 2 [28]

\[ E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhibitor}}) \] .......................... (1)

Where \( E_{\text{total}} \) is the total energy of the surface and adsorbed inhibitor molecule, \( E_{\text{surface}} \) is the energy of the surface without the inhibitor and \( E_{\text{inhibitor}} \) is the energy of the adsorbed inhibitor on the surface. The binding energy of the inhibitor molecule is the negative value of interaction energy [30].

\[ E_{\text{binding}} = -E_{\text{interaction}} \] ........................................... (2)

Table 1. IUPAC name, Molecular structure, Abbreviation and Molar mass of the studied molecules.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Structure</th>
<th>Abbreviation</th>
<th>Molar mass (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylpyrazine</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>MP</td>
<td>94.11</td>
</tr>
<tr>
<td>2-aminopyrazine</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>AP</td>
<td>95.1</td>
</tr>
<tr>
<td>2-amino-5-bromopyrazine</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>ABP</td>
<td>174</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1 Molecular Orbital Energy Level Calculations

To determine a relationship between inhibitors and their corresponding inhibition efficiency, quantum chemical calculation are used herein. Optimised geometric structures and Mulliken spin density plots of HOMO and LUMO for the inhibitors were studied which supported the corrosion inhibition efficiency obtained from experimental results [13]. Calculations were performed with DFT using B3LYP function. The chemical structure of the molecules under investigation were presented in Table 1 and their optimised geometric structures, frontier molecular orbital densities are presented in Figures 1-3. Quantum
Table 2. Calculated quantum chemical parameters of the studied inhibitors.

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$E_{HOMO}$ (eV)</th>
<th>$E_{LUMO}$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>$\mu$ (Debye)</th>
<th>$I = -\frac{E_{HOMO}}{E_{LUMO}}$</th>
<th>$A = -\frac{E_{LUMO}}{E_{HOMO}}$</th>
<th>$\chi$</th>
<th>$\eta$</th>
<th>$\Delta N$</th>
<th>Inhibition efficiency$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>-7.0125</td>
<td>-1.6127</td>
<td>5.3998</td>
<td>0.7456</td>
<td>7.0125</td>
<td>1.6127</td>
<td>4.3126</td>
<td>2.6999</td>
<td>0.4976</td>
<td>83.3</td>
</tr>
<tr>
<td>AP</td>
<td>-6.1266</td>
<td>-1.3303</td>
<td>4.7963</td>
<td>3.1176</td>
<td>6.1266</td>
<td>1.3303</td>
<td>3.7284</td>
<td>2.3981</td>
<td>0.6821</td>
<td>85.3</td>
</tr>
<tr>
<td>ABP</td>
<td>-6.1561</td>
<td>-1.6044</td>
<td>4.5517</td>
<td>5.7059</td>
<td>6.1561</td>
<td>1.6044</td>
<td>3.8802</td>
<td>2.2758</td>
<td>0.6854</td>
<td>89.8</td>
</tr>
</tbody>
</table>

$^a$ Values obtained from Ref [13]

Table 3. Calculated Fukui functions for the three inhibitor molecules.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Atom</th>
<th>$f_k^+$</th>
<th>$f_k^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>C (1)</td>
<td>0.101</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>N (2)</td>
<td>0.179</td>
<td>0.193</td>
</tr>
<tr>
<td></td>
<td>C (3)</td>
<td>0.107</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>C (4)</td>
<td>0.084</td>
<td>0.068</td>
</tr>
<tr>
<td></td>
<td>N (5)</td>
<td>0.171</td>
<td>0.192</td>
</tr>
<tr>
<td></td>
<td>C (6)</td>
<td>0.108</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>C (7)</td>
<td>0.025</td>
<td>0.032</td>
</tr>
<tr>
<td></td>
<td>C (1)</td>
<td>0.078</td>
<td>0.137</td>
</tr>
<tr>
<td></td>
<td>N (2)</td>
<td>0.178</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td>C (3)</td>
<td>0.137</td>
<td>0.113</td>
</tr>
<tr>
<td></td>
<td>C (4)</td>
<td>0.070</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>N (5)</td>
<td>0.153</td>
<td>0.084</td>
</tr>
<tr>
<td></td>
<td>C (6)</td>
<td>0.120</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>N (7)</td>
<td>0.050</td>
<td>0.187</td>
</tr>
<tr>
<td>ABP</td>
<td>C (1)</td>
<td>0.055</td>
<td>0.088</td>
</tr>
<tr>
<td></td>
<td>N (2)</td>
<td>0.158</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td>C (3)</td>
<td>0.141</td>
<td>0.099</td>
</tr>
<tr>
<td></td>
<td>C (4)</td>
<td>0.064</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td>N (5)</td>
<td>0.146</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>C (6)</td>
<td>0.121</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>N (7)</td>
<td>0.047</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>Br (8)</td>
<td>0.103</td>
<td>0.212</td>
</tr>
</tbody>
</table>

Table 4. Interaction and Binding energies between the inhibitor molecules and Fe (0 0 1) plane.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$E_{interaction}$ (kcal/mol)</th>
<th>$E_{binding}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe + MP</td>
<td>-49.007</td>
<td>49.007</td>
</tr>
<tr>
<td>Fe + AP</td>
<td>-50.168</td>
<td>50.168</td>
</tr>
<tr>
<td>Fe + ABP</td>
<td>-59.162</td>
<td>59.162</td>
</tr>
</tbody>
</table>

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chemical parameters, such as $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, energy gap ($\Delta E$), dipole moment ($\mu$), electronegativity ($\chi$), global hardness ($\eta$) and fraction of electron transferred ($\Delta N$) are tabulated in Table 2.

The adsorption ability of the molecule over metal surface is related to their FMO (frontier molecular orbital) $i.e.$ highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) $[31,32]$. HOMO is associated with capability of a molecule to donate electrons whereas LUMO indicates its capability to accept electrons. From Figures 1-3, it can be seen that the electronic density in HOMO and LUMO on the entire area of each molecule are quite uniform which is due to its $\pi$-electron cloud density. In MP molecule, the HOMO density is mainly distributed on the pyrazine ring (Figure 1 (b)), which is attributed to the presence of lone pairs on the nitrogen atom of the pyrazine ring. Similarly for AP (Figure 2 (b)), higher HOMO density is mainly distributed on the pyrazine ring and the nitrogen atom of the amino group. However for ABP (Figure 3 (b)), due to the presence of additional bromide substituent on the pyrazine ring it contains much higher HOMO electron density than MP and AP molecules. Thus, the preferred active sites for electron donation in MP, AP and ABP are mainly located in the pyrazine ring and its different substituents. The LUMO density on the C-C region and the nitrogen atoms of the pyrazine ring are higher (Figures 1 (c)–3 (c)), making them preferred active sites for accepting electrons. Thereby, after analysing the electronic distribution of HOMO and LUMO it is reasonable to say that the ABP molecule acts as the best corrosion inhibitor among the three discussed molecules. We have also analysed the HOMO, LUMO spin density plots for the inhibitor molecules by Dmol$^3$ module in Material studio™ and the results are in well agreement with the same using ORCA module. Quantum chemical parameters as well as frontier molecular orbital (FMO) densities resulted from Dmol$^3$ module are presented in Table S1 and Figures S1-S3 respectively.

$E_{\text{HOMO}}$ represents the tendency of inhibitor towards the donation of electrons to the unoccupied d-orbitals of metals. Higher the HOMO energy of the inhibitor better the tendency of it towards donation of electron to the acceptor molecule with low lying empty orbital. Therefore higher value of $E_{\text{HOMO}}$ implies that better the donating capability of inhibitor and therefore better the inhibition efficiency. The energy of lowest unoccupied molecular orbital ($E_{\text{LUMO}}$) signifies the ability of molecules to accept electrons from the metal surface. Thus lower is the value of $E_{\text{LUMO}}$ better will be its inhibition efficiency $[33]$. Thus the binding ability of inhibitor on the metal surface increases with increasing energy of $E_{\text{HOMO}}$ and decreasing the energy of $E_{\text{LUMO}}$. In the same way, lower value of the energy gap $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ will render good inhibition efficiency, because the energy to remove an electron to last occupied molecular orbital will be low $[34]$. In summary, terms which are involved in the frontier MO, could provide the domnintive contribution, as because inverse dependence of stabilization energy on orbital energy difference. Organic compounds, those have the capability to not only donate electrons to unoccupied orbitals of the metal, but has equal possibility to accept free electrons from metal are best corrosion inhibitors.

Theoretical Quantum chemistry calculations with neutral form of inhibitors could be a good approach to authenticate the inhibitor efficiency whatever obtained from experimental results. In recent time, experimental researchers Li et. al. indicates that the inhibition efficiency increases in the order of MP < AP < ABP $[13]$. This experimental outcome could be validated by theoretical quantum chemical outcomes. From Table 2 it could be seen that $E_{\text{HOMO}}$ values of the three pyrazine ligands obeys the order AP > ABP > MP, while $E_{\text{LUMO}}$ values of the three selected inhibitors follows the order of MP < ABP < AP. Obviously the sequences of $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ are not in complete agreement with the order of experimental inhibition efficiency, which suggests that there exist some complex nature of interaction (both chemisorption and physisorption) $[35]$ in the corrosion inhibition process. This is satisfactory judging from the values of $\Delta G^0$ obtained from the experimental work lies between -28.3 to -29.7 kJ mol$^{-1}$ $[13]$. It has been also reported in the literature that the values of $\Delta G^0$ lies in this above mentioned range.
Figure 4. Fukui functions for MP molecule calculated by DFT (Dmol$^3$). (a) Geometry optimized structure, (b) Nucleophilic and (c) Electrophilic Fukui functions.

Figure 5. Fukui functions for AP molecule calculated by DFT (Dmol$^3$). (a) Geometry optimized structure, (b) Nucleophilic and (b) Electrophilic Fukui functions.

Figure 6. Fukui functions for ABP molecule calculated by DFT (Dmol$^3$). (a) Geometry optimized structure, (b) Nucleophilic and (b) Electrophilic Fukui functions.
generally indicates adsorption may involve mixed type adsorption [36]. According to the frontier orbital theory $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ are mainly responsible for reaction of reactants. Thus the smaller the gap ($\Delta E$) between $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$, more it is appropriate to donate and accept electrons. The $\Delta E$ values of the three inhibitors (Table 2) increase in the order ABP $<$ AP $<$ MP, suggesting that ABP molecule has the strongest ability to form co-ordinate bonds to the vacant d-orbitals of metal by donating and accepting electrons. Moreover increasing values of dipole moment has been reported to facilitate adsorption by influencing the transport process through adsorbed layer [37]. The values of dipole moment follows the order ABP $>$ AP $>$ MP, which further indicates that the results are in good agreement with the results obtained from experimental work.

Electron density distributions was carried out by Natural bond orbital (NBO) analysis. In calculating the chemical reactivity parameters this electron density plays a very important role. Global reactivity includes electro negativity, $\chi$, which is defined in the finite difference approximation as the negative of the chemical potential $\mu$, $\chi = -\mu$. The ionization potential ($I$) and electron affinity ($A$) of inhibitor molecules can be calculated by the application of Koopmans' theorem [38]. This theorem shows a clear relationship between the HOMO and ionization potential; LUMO and electron affinity of the concerned molecule respectively. There are no formal authentication of this theorem is present within DFT, however its validity accepted since long back. The obtained ionization potential and electron affinity values are hereby used to get the electronegativity ($\chi$) and global hardness ($\eta$) of the molecule. These are related to ionization potential and electron affinity by the following formula:

$$\chi = \frac{I + A}{2}$$

The global hardness $\eta$ defined as:

$$\eta = \frac{I - A}{2}$$

$I$ and $A$ are related to $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ as follows:

$$I = - E_{\text{HOMO}}$$

$$A = - E_{\text{LUMO}}$$

The fraction of electrons transferred from the inhibitor molecule to the metallic surface ($\Delta N$) was calculated by Pearson method [39]. The difference in electronegativities between the two systems (metallic surface and inhibitor molecule) is responsible for corresponding electron transfer. Electron flow will happen from the molecule with low electronegativity towards that of higher value until the chemical potentials are same. According to Pearson, in order to calculate the fraction of electron transferred, absolute electronegativity of bulk iron was used $\chi_{\text{Fe}} = 7 \text{eV}$ [39] and global hardness of $\eta_{\text{Fe}} = 0$, by assuming that for a metallic bulk $I = A$ [40] because they are softer than the neutral metallic atoms. The fraction of electrons transfers to the metallic surface is calculated as follows:

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})}$$

From the Table 2 it is observed that ABP molecule has a lowest value of global hardness. The fraction of electron transfer is also comparatively higher for ABP molecule in comparison to AP and MP. It has been reported in literature that lower value of hardness and higher value of fraction of electron transferred enhances inhibition efficiency [41]. Thus higher inhibition effect of ABP compared to AP and MP were observed and authenticated.
3.1.1 Local Reactivity of the Selected Corrosion Inhibitors

To establish the active site of an inhibitor molecule, three influencing and controlling factors: neutral atomic charge, distribution of frontier molecular orbital and Fukui indices have to be considered. Local reactivity is analyzed by means of the condensed Fukui function. Condensed Fukui functions allow us to distinguish each part of the molecule on the basis of its distinct chemical behaviour due to the different substituent functional groups. The nucleophilic and electrophilic attack is controlled by the maximum values of $f^+_k$ and $f^-_k$. The calculated Fukui indices for nucleophilic and electrophilic attack for
the three selected inhibitors are tabulated in Table 3 (only C, N, O and Br are quoted) and their active sites are presented in Figures 4-6. It can be seen from Table 3 that the largest values of $f_k^-$ are located on the N(2) and N(5) atoms of MP molecule, which indicates that these two atoms prefer to form a chemical bond by donation of electrons to the metal surface. While the largest values of $f_k^+$ are located on the C(1), N(2), C(3), N(5) and C(6) atoms, which further suggest that these atoms are responsible to form a back bond by the acceptance of electron from the metal surface. However, when the methyl group in the pyrazine ring is replaced by amido group, Fukui indices of N(2) and N(5) atoms decreases where as C(1), C(3) and N(7) atoms increase, suggests that AP molecule donates its electron through these sites and accepts electron through N(2), C(3), N(5) and C(6) sites. Whereas ABP molecule donates its electron through C(3), N(7) and Br(8) sites and accept electron through N(2), C(3), N(5) and Br(8) atomic sites. Based on the above discussion, it can be concluded that ABP molecule has many active centres for adsorption on iron surface. These are areas containing C, N and Br atoms and are the most probable sites for electron relay to the iron surface.

![Energy fluctuation curves obtained from molecular dynamics simulation for (a) MP, (b) AP and (c) ABP.](image)

**Figure 8.** Energy fluctuation curves obtained from molecular dynamics simulation for (a) MP, (b) AP and (c) ABP.

### 3.2 Molecular Dynamics Simulation

Molecular dynamics simulations were performed to study the adsorption behaviour of specific inhibitor molecules on Fe (0 0 1) surface. The geometry optimization for all three selected studied
inhibitors is carried out using an iterative process, where atomic coordinates are adjusted until and unless the total energy of individual structure reaches the minimum energy, i.e., it corresponds to a local minimum in the potential energy surface. In this study, three selected inhibitors (MP, AP and ABP) have been placed on the Fe (0 0 1) surface to find out the most low energy adsorption sites along with their suitable configuration. The Figures 7 and 8 show temperature and energy fluctuation curve with respect to the simulation time. Equilibration of the system is confirmed by the steady average values of temperature and energy [42]. The close contacts between the inhibitor molecules and iron surface as well as the best adsorption configurations for the compounds were depicted in Figure 9. The calculated interaction and binding energy obtained from molecular dynamics simulation were presented in Table 4.

Interaction energy ($E_{\text{interaction}}$) between Fe (0 0 1) surface and inhibitor molecules can be evaluated according to the Equation (1) by single point energy calculation. The calculated interaction energy values of the adsorption systems were -49.007, -50.168 and -59.162 kcal mol$^{-1}$ for MP, AP and ABP respectively. The larger negative values of interaction energy can be attributed to the strong adsorption between the inhibitor molecules and the iron surface [43]. The calculated values of interaction energy during the simulation process revealed that ABP has the highest interaction energy among the three tested inhibitors. From the theoretical point of view, high values of interaction energy indicate that ABP molecule will give highest inhibition efficiency. The calculated inhibition efficiency of the studied inhibitors decrease in the order: ABP > AP > MP. Moreover, the higher magnitude of binding energy for ABP inhibitor, presented in

Figure 9. Equilibrium adsorption configurations of inhibitors MP (a and d), AP (b and e) and ABP (c and f) on Fe (0 0 1) surface obtained by molecular dynamics simulations. Top: top view, bottom: side view.
Table 4 also suggests a more stable adsorption system for ABP with higher inhibition efficiency [44]. The relative inhibition efficiency of the molecules can be drawn from the values of interaction energy as well as binding energy. The stability of the inhibitor molecules and its inhibition efficiency are ranked as ABP > AP > MP. These results are all in good agreement with the results obtained from experimental work [13] as well as from theoretical quantum chemical calculations. In this way, we may infer that among the three studied inhibitors, ABP can be best adsorbed on the Fe (0 0 1) surface through the pyrazine heterocyclic ring and the side chain (bromo and amino side). The exposed Fe surface can be made corrosion resistant in presence of the pyrazine moiety and side chains.

4. CONCLUSION

We may conclude that through Quantum chemical (DFT) calculations a correlation between parameters related to the electronic structure of three substituted pyrazines and their potential to inhibit the corrosion process in particular acid medium could be established. It is also found that the calculated molecular parameters are all in good agreement with the experimental inhibition efficiency, confirming the reliability of the empirical and quantum chemical method employed herein. From theoretical experimentation it was found that the order of inhibition efficiency is ABP > AP > MP, which agrees well with the experimental outcomes evaluated by combination of quantum chemistry calculation along with molecular dynamics simulation. It is noteworthy that this study compares the results obtained from three different domains e.g. from quantum chemical calculation which is based on quantum chemistry, molecular dynamics simulation which originates from classical physics and wet chemical experiments. Coherence among these results is an interesting aspect of this work. The researchers here have shown that molecular modeling might be an effective, time saving and cost effective approach to assess the inhibition performance, which has potential application in designed architect of new organic corrosion inhibitor molecules and to cross check their corrosion inhibition performance well in advance without doing the hardcore synthetic work.

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SUPPORTING INFORMATION

Table S1 and Figures S1-S3 are included in the supporting information.

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*The authors declare no conflict of interest*

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