Studies on adsorption and corrosion inhibitive properties of quinoline derivatives on N80 steel in 15% hydrochloric acid

K.R. Ansari1*, Sowmya Ramkumar2, D. Nalini2 and M.A. Quraishi1

Abstract: This paper deals with the N80 steel corrosion protection study in 15% HCl which was carried by three quinoline derivatives namely 3-acetyl-1-(4-methylbenzylideneamino) quinolin-2-one (AQ-1), 3-acetyl-1-(4 hydroxy benzylideneamino) quinolin-2-one (AQ-2), 3-acetyl-1-(3-nitrobenzylideneamino) quinolin-2(1H)-one (AQ-3) using gravimetric, electrochemical, and quantum chemical studies. Tafel polarization showed that AQs are mixed type inhibitors but dominantly affect cathodic reaction more. The observed results reveal that AQ-1 is the best inhibitor. All the three inhibitors were found to obey the Langmuir adsorption isotherm. Scanning electron microscopy (SEM) micrographs supports the protection of the N80 steel by AQs. Quantum chemical study reveals that the inhibitors have a tendency to get protonated and this protonated form has greater tendency to get adsorbed onto the N80 steel surface.

1. Introduction
Hydrochloric acid is more commonly used for acidization of oil wells in order to enhance the oil production. In general, 15% HCl is forced into the oil well through the N80 steel made tubing, in order to open the bore channels and hence increases the oil flow. However, this process has a negative impact i.e. it severely causes the corrosion of N80 steel. Thus, protection of N80 steel from corrosion...
can be done using corrosion inhibitors. Generally, commonly known inhibitors are organic compounds (Amin, Khaled, Mohsen, & Arida, 2010; Ansari & Quraishi, 2015a; Ansari, Quraishi, & Singh, 2014; Ansari, Quraishi, & Singh, 2015b; Ansari, Yadav, Ebenso, & Quraishi, 2012; Geethamani & Kasthuri, 2015).

In literature most of the organic compounds are showing their inhibition effects at lower acid concentration (Ebenso, Obot, & Murulana, 2010; Moretti, Guidi, & Fabris, 2013; Solmaz, 2014). Today’s research in corrosion is mainly focused toward the use of green inhibitors (Ansari & Quraishi, 2015c). So, implicating the above said statement, we have synthesized the quinoline derivatives which are showing various biological actively like antitumor, anti-inflammatory, antiplatelet, antiulcer, antioxidant, and antidepressant activities (Kumar, Fernandes, & Kumar, 2014).

Recently, quantum chemical studies have become a perfect tool for determining the molecular structure as well as elucidating the electronic structure and reactivity (Musa, Kadhum, Mohamad, & Takriff, 2011).

The present paper reports the inhibition action of three quinoline derivatives namely 3-acetyl-1-(4-methylbenzylideneamino) quinolin-2-one (AQ-1), 3-acetyl-1-(4 hydroxy benzylideneamino) quinolin-2-one (AQ-2), 3-acetyl-1-(3-nitrobenzylideneamino) quinolin-2(1H)-one (AQ-3), using gravimetric measurement, electrochemical impedance spectroscopic (EIS), Tafel polarization, SEM, and Quantum studies in both neutral and protonated forms.

2. Experimental

2.1. Materials

The test solution i.e. 15% HCl (v/v) was prepared by diluting 37% analytical grade HCl with double-distilled water. The composition of N80 steel sample (wt%) used is as follows: C: 0.31; Si: 0.19; Mn: 0.92; P: 0.010; S: 0.008; Cr: 0.2; and balance Fe. N80 steel strips dimensions used for gravimetric and electrochemical experiments are 5.0 cm × 2.5 cm × 0.2 cm and 2.0 cm × 1.0 cm × 0.025 cm, respectively. The N80 steel strips were polished using SiC abrasive papers having grades ranging from 600 to 1,200, degreased with acetone and lastly dried at room temperature.

2.2. Inhibitors

The investigated organic compounds were synthesized according to the laboratory procedure reported previously (Kumar et al., 2014). The chemical structure, abbreviations, and IUPAC names are given in Table 1.

2.3. Gravimetric experiments

The corrosion rate \( C_R \) (mg cm\(^{-2}\) h\(^{-1}\)) was calculated from the following equation (Ansari & Quraishi, 2015b).

\[
C_R = \frac{W}{At}
\]  

where \( W \) is the weight loss of a N80 steel strip, \( A \) is the total area of a N80 steel strip, and \( t \) is immersion time (6 h).

The surface coverage (\( \theta \)) and inhibition efficiency (\( \eta \% \)) were calculated using following equations (Ansari & Quraishi, 2015d):

\[
\theta = \frac{C_R - C_{R(i)}}{C_R}
\]  

\[
\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100
\]
where \( C_r \) and \( C_{ri} \) are corrosion rates (mg cm\(^{-2}\) h\(^{-1}\)) of N80 steel in the absence and presence of inhibitors, respectively.

### 2.4. Electrochemical measurements

A three-electrode cell assembly was used, where N80 steel strip with an exposed area of 1 cm\(^2\) was used as working electrode, graphite rod as counter, and saturated calomel as reference electrodes. All measurements were carried out using Gamry Potentiostat/Galvanostat (Model G-300) and data analysis was carried out using Echem Analyst 5.0 software package. All electrochemical experiments were conducted at 308 K temperature.

The potentiodynamic polarization measurements were performed by changing the electrode potential automatically from −250 to +250 mV vs. SCE at open circuit potential (OCP) at a scan rate of 1 mVs\(^{-1}\).

EIS measurements were carried out using AC signal of amplitude 10 mV peak to peak in the frequency range of 100 kHz to 0.01 Hz at OCP. All electrochemical experiments were done after immersing for 30 min in 15% HCl in the absence and presence of AQs.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-acetyl-1-(4-methylbenzylideneamino) quinolin-2(1H)-one (AQ-1)</td>
<td><img src="AQ1.png" alt="Structure" /></td>
</tr>
<tr>
<td>3-acetyl-1-(4-hydroxybenzylideneamino) quinolin-2(1H)-one (AQ-2)</td>
<td><img src="AQ2.png" alt="Structure" /></td>
</tr>
<tr>
<td>3-acetyl-1-(3-nitrobenzylideneamino) quinolin-2(1H)-one (AQ-3)</td>
<td><img src="AQ3.png" alt="Structure" /></td>
</tr>
</tbody>
</table>

Table 1. Molecular structure and analytical data of AQs

where \( C_r \) and \( C_{ri} \) are corrosion rates (mg cm\(^{-2}\) h\(^{-1}\)) of N80 steel in the absence and presence of inhibitors, respectively.
2.5. Surface morphology
Surface analysis was carried out using SEM in order to find out the morphological changes occurring on the N80 steel surface in the absence and presence of AQs. SEM analysis was carried out by first exposing the N80 steel samples to 15% HCl solution in the absence and presence of optimum concentration (200 mg/L) of AQs for 6 h at 308 K, respectively. The SEM was performed by a Ziess SUPRA 40 instrument model, with magnification of 5k×.

2.6. Quantum chemical study
These three inhibitor molecules have been fully optimized using B3LYP Density Functional Theory formalism (DFT) with 6-31 G (d, p) basis set using Gaussian-03 (Frisch et al., 2007). The following quantum chemical parameters were studied: Energy of the Highest Occupied Molecular Orbital (\(E_{\text{HOMO}}\)), Energy of the Lowest Unoccupied Molecular Orbital (\(E_{\text{LUMO}}\)), Energy gap between HOMO and LUMO (\(\Delta E\)), and dipole moment (\(\mu\)).

3. Results and discussion

3.1. Gravimetric measurements

3.1.1. Effect of inhibitor concentration
The concentration of the AQs was taken in the range of 50–200 mg L\(^{-1}\) and the obtained inhibition efficiency is shown in Figure 1(a). Figure 1(a) reveals that inhibition efficiency increases with increase in inhibitor concentration.
3.1.2. Effect of temperature
The temperature range of 308–328 K was used to study the effect of temperature and the temperature effect over the inhibition efficiency is shown in Figure 1(b). It could be observed from Figure 1(b) that as the temperature is increased, the inhibition efficiency is going to decrease.

The calculation of activation energy \( (E_a) \) was carried out using the Arrhenius plots, which is a plot of corrosion rate \( [C_R (mg \cdot cm^{-2} \cdot h^{-1})] \) vs. \( T \) and could be given by the following relation (Ansari, Quraishi, & Singh, 2015a):

\[
C_R = A \exp \left( \frac{-E_a}{RT} \right)
\]

(4)

where \( E_a \) is the activation energy, \( T \) is the absolute temperature, \( A \) is the Arrhenius pre-exponential constant, and \( R \) is the universal gas constant. \( E_a \) values were obtained from the slope of the Arrhenius plots (Figure 1(c)). The values of \( E_a \) in the absence of AQs are lower than in their presence i.e. 34.58 kJ mol\(^{-1}\) (blank) and 73.16 kJ mol\(^{-1}\) (AQ-1), 64.14 kJ mol\(^{-1}\) (AQ-2), and 50.26 mol\(^{-1}\) (AQ-3), respectively. Thus, the higher values of \( E_a \) in the presence of AQs reveal that adsorption of AQs occurs over the N80 steel surface, which increases the energy barrier for the corrosion process (Ansari et al., 2012).

3.1.3. Adsorption isotherm
The mechanism of interaction between the AQs and the N80 steel surface was studied by using adsorption isotherm. In the present study, three adsorption isotherms have been studied i.e. the Langmuir, Frumkin, and Temkin. These isotherms can be related with the surface coverage (\( \theta \)) with
inhibitor (AQs) concentrations according to the following equations (Yadav, Chauhan, Ahamad, & Quraishi, 2013):

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \text{(Langmuir)}
\]

\[
\exp(-2a\theta) = KC \quad \text{(Temkin)}
\]

\[
\ln\left(\frac{\frac{\theta}{C(1-\theta)}}{\frac{1}{K_{ads}} + C}\right) = \ln K + 2a\theta \quad \text{(Frumkin)}
\]

The correlation coefficient \(R^2\) and slope values for the studied isotherms are given in Table 2. It could be observed from Table 2 that the correlation coefficient \(R^2\) and slope values for the Langmuir isotherm is least deviated from unity as compared to other isotherms (Table 2). So, the Langmuir adsorption isotherm is the best fit in the present case and is shown in Figure 1(d). The standard free energy of adsorption \(\Delta G_{ads}\) and equilibrium constants \(K_{ads}\) are correlated according to the equation (Ansari & Quraishi, 2014):

\[
\Delta G_{ads} = -RT \ln(55.5K_{ads})
\]

where \(R\) is the gas constant and \(T\) is the absolute temperature. The value of 55.5 is the concentration of water in solution in mol L\(^{-1}\).

Using the intercept \(K_{ads}\) values were calculated and are given as follows 1.24 \times 10^4 M\(^{-1}\) (AQ-1), 1.10 \times 10^4 M\(^{-1}\) (AQ-2), and 9.4 \times 10^4 M\(^{-1}\) (AQ-3). And also the \(\Delta G_{ads}\) adsorption values are 34.43 kJ mol\(^{-1}\) (AQ-1), 34.12 kJ mol\(^{-1}\) (AQ-2), and 33.73 kJ mol\(^{-1}\) (AQ-3). This \(\Delta G_{ads}\) adsorption values are less than −40 kJ mol\(^{-1}\) but more than −20 kJ mol\(^{-1}\), showing that PZs adsorption are both physical and chemical (Ansari & Quraishi, 2015d).

### 3.2. Electrochemical measurements

#### 3.2.1. Electrochemical impedance spectroscopy

The Nyquist plots for N80 steel in 15% HCl in the absence and presence of AQs at their optimum concentrations (200 mg/L) at 308 K are shown in Figure 2(a). The inspection of the Nyquist plots reveals that in the presence of AQs, the diameter of the semicircle is larger than in their absence. The EIS spectra were analyzed using the equivalent circuit shown in Figure 2(b), which consists of a parallel combination of the charge transfer resistance \(R_{ct}\) and the constant phase element (CPE), both in series with the solution resistance \(R_s\). CPE is introduced instead of pure double-layer capacitance to give more accurate fit as the double layer at interface does not behave as an ideal capacitor. Fitness accuracy of equivalent circuit was checked by plotting the simulated Nyquist and bode

### Table 2. Adsorption parameters for AQs calculated from different adsorption isotherms for N80 steel in 15% HCl solution at 308 K

<table>
<thead>
<tr>
<th>Adsorption isotherm</th>
<th>Inhibitor</th>
<th>Correlation coefficient</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temkin</td>
<td>AQ-1</td>
<td>0.995</td>
<td>0.186</td>
</tr>
<tr>
<td></td>
<td>AQ-2</td>
<td>0.995</td>
<td>0.197</td>
</tr>
<tr>
<td></td>
<td>AQ-3</td>
<td>0.996</td>
<td>0.190</td>
</tr>
<tr>
<td>Frumkin</td>
<td>AQ-1</td>
<td>0.667</td>
<td>3.089</td>
</tr>
<tr>
<td></td>
<td>AQ-2</td>
<td>0.658</td>
<td>2.148</td>
</tr>
<tr>
<td></td>
<td>AQ-3</td>
<td>0.196</td>
<td>0.513</td>
</tr>
<tr>
<td>Langmuir</td>
<td>AQ-1</td>
<td>0.998</td>
<td>0.912</td>
</tr>
<tr>
<td></td>
<td>AQ-2</td>
<td>0.998</td>
<td>0.919</td>
</tr>
<tr>
<td></td>
<td>AQ-3</td>
<td>0.997</td>
<td>0.967</td>
</tr>
</tbody>
</table>
plots and is shown in Figure 2(c and d). The inhibition efficiency (η %) was calculated from charge transfer resistance values obtained from impedance measurements using the following relation:

\[ \eta \% = \left( 1 - \frac{R_{ct}}{R_{ct(i)}} \right) \times 100 \]  

(9)

The impedance of the CPE can be given as follows (Xu et al., 2014):

\[ Z_{\text{CPE}} = Y_0^{-1}(j\omega)^{-n} \]  

(10)

where \( Y_0 \) is the amplitude comparable to a capacitance, \( j \) is the square root of \(-1\), \( \omega \) is angular frequency, and \( n \) is the phase shift.

Double-layer capacitance (\( C_{\text{dl}} \)) can be calculated as follows

\[ C_{\text{dl}} = \frac{Y\omega^{n-1}}{\sin (n\pi/2)} \]  

(11)

where \( \omega \) is the angular frequency (\( \omega = 2\pi f_{\text{max}} \)) at which the imaginary part of impedance (\( -Z_{\text{im}} \)) is maximal and \( n \) is the phase shift.

Figure 2. (a) Nyquist plots for mild steel in 15% HCl in the absence and presence of optimum concentration of inhibitors at 308 K, (b) Equivalent circuit model used to fit the EIS data, (c) and (d) Fitted Nyquist and Bode plot, (e) Bode (log \( f \) vs. log \( |Z| \)) and phase angle (log \( f \) vs. \( \alpha \)) plots of impedance spectra for N80 steel in 15% HCl in the absence and presence of optimum concentration of inhibitors at 308 K.
The data shown in Table 3 reveal that the value of $R_{ct}$ increases with the addition of AQs as compared to the blank solution, the increase in $R_{ct}$ value is attributed to the formation of a protective film at the metal/solution interface. The $C_{dl}$ values decrease in the presence of AQs, which may arise due to a decrease in local dielectric constant and/or to an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules are adsorbed at the metal/solution interface (Qu, Jiang, Bai, & Li, 2007).

The single peak obtained in Bode plots (Figure 2(e)) for both inhibitors (AQs) indicates that the electrochemical impedance measurements were fitted well in one time-constant equivalent model with CPE.

Moreover, there is only one phase maximum in Bode plots for both inhibitors, which indicates only one relaxation process, which would be the charge transfer process, taking place at the metal–electrolyte interface. Also, Figure 2(e) shows that the impedance value in the presence of both inhibitors is larger than in the absence of inhibitors.

These mean that the corrosion rate is reduced in the presence of the inhibitors.

<table>
<thead>
<tr>
<th>$C_{inh}$ (mg L$^{-1}$)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$n$</th>
<th>$Y_0$ (μF/cm$^2$)</th>
<th>$C_{dl}$ (μF/cm$^2$)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.82</td>
<td>4.58</td>
<td>0.755</td>
<td>603</td>
<td>134.24</td>
<td>-</td>
</tr>
<tr>
<td>AQ-1</td>
<td>1.417</td>
<td>155.88</td>
<td>0.877</td>
<td>127.8</td>
<td>68.37</td>
<td>97.06</td>
</tr>
<tr>
<td>AQ-2</td>
<td>1.076</td>
<td>106.82</td>
<td>0.824</td>
<td>148.4</td>
<td>70.17</td>
<td>95.71</td>
</tr>
<tr>
<td>AQ-3</td>
<td>1.03</td>
<td>52.77</td>
<td>0.818</td>
<td>164.2</td>
<td>74.84</td>
<td>91.32</td>
</tr>
</tbody>
</table>
3.2.2. Tafel polarization

The Tafel polarization curves of N80 steel at optimum concentration of AQs are shown in Figure 3. All the Tafel polarization parameters i.e. corrosion potential ($E_{corr}$), cathodic Tafel slope ($\beta_c$), anodic Tafel slope ($\beta_a$), and corrosion current density ($I_{corr}$) obtained from the extrapolation of Tafel lines are given in Table 4. The percentage of inhibition efficiencies ($\eta$ %) are calculated using the following equation:

$$\eta\% = \left(1 - \frac{I_{corr}}{I_{corr(i)}}\right) \times 100$$

where $I_{corr}$ and $I_{corr(i)}$ are the uninhibited and inhibited corrosion current densities, respectively.

Table 4 shows that difference between cathodic Tafel slope ($\beta_c$) and anodic Tafel slope ($\beta_a$) is not much higher, which indicates that, AQs control both cathodic and anodic.

The polarization curves reveal that cathodic currents are reduced, but no such definite trend is observed in anodic curve as the AQs are added and also the shifts in $E_{corr}$ occurs toward more negative direction with respect to blank. The difference of calculated $E_{corr}$ of blank and inhibitor is less than 85 mV. So, the inhibitor is said to be mixed type. However, the above said statement on the $E_{corr}$ shift concludes that the inhibitor is mixed type but dominantly affecting cathodic reaction more (Ansari, Quraishi, & Singh, 2015c). The cathodic Tafel lines are parallel (Figure 3), showing that hydrogen evolution mechanism with the addition of AQs has not modified, and hydrogen ions reduction mainly takes place through charge transfer mechanism (Issaadi et al., 2011). It can be observed from Table 4 that the $I_{corr}$ values in presence of AQs decreases. These mean that the AQs are adsorbed onto the N80 steel and reduced the corrosion rate.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$E_{corr}$ (mV/SCE)</th>
<th>$I_{corr}$ (μA/cm²)</th>
<th>$\beta_a$ (mV/dec)</th>
<th>$-\beta_c$ (mV/dec)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-443</td>
<td>3,201</td>
<td>85.7</td>
<td>100.8</td>
<td></td>
</tr>
<tr>
<td>AQ-1</td>
<td>-495</td>
<td>88.3</td>
<td>97.7</td>
<td>116.3</td>
<td>97.24</td>
</tr>
<tr>
<td>AQ-2</td>
<td>-481</td>
<td>137</td>
<td>68.4</td>
<td>100.1</td>
<td>95.72</td>
</tr>
<tr>
<td>AQ-3</td>
<td>-498</td>
<td>265</td>
<td>93.9</td>
<td>121.5</td>
<td>91.72</td>
</tr>
</tbody>
</table>

Figure 3. Tafel curves for N80 steel in 15% HCl in the absence and presence of optimum concentration of inhibitor at 308 K.
3.3. Surface analysis: SEM
The surface analysis was carried out for the N80 steel immersed in 15% M HCl in the absence (Figure 4(a)) and presence of optimum concentration (200 mg L\(^{-1}\)) of AQs (Figure 4(b–d)) after 6 h by SEM analysis. In the absence of inhibitor significant damage of N80 steel surface is observed (Figure 4(a)), indicating its severing corrosion. However, in the presence of AQs (Figure 4(b–d)), the surface is protected, which is supported by the smooth N80 steel surface morphology. So in presence of AQs, corrosion is restricted because of the adsorption of AQs molecules. This result is in agreement with the results obtained by electrochemical measurement.

3.4. Quantum chemistry method

3.4.1. Non-protonated AQs
All quantum chemical parameters are given in Table 5 for AQs in their neutral forms. The optimized geometries (with Mulliken charges), HOMO, and LUMO distributions of AQs in their non-protonated form are shown in Figures 5(a–c) and 6(a–f). It is reported in the literature that interaction between the reactants takes place via the involvement of frontier molecular orbitals i.e. HOMO and LUMO. HOMO energy is associated with electron donation ability of the inhibitor. So, higher the HOMO energy, more easily the electrons can be donated by the inhibitor to the unoccupied d-orbitals of the metal. However, LUMO energy is associated with the electron acceptation tendency of the molecule. Thus, lower the LUMO energy, more easily inhibitor molecule can accept electrons from the metal. Consequently, the value of the energy gap, \(\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}\), represents the reaction tendency of the
inhibitor i.e. the lower its value, higher would be the inhibition efficiency. The dipole moment ($\mu$) is also an important parameter. However, in literature there is no correlation exit between the dipole moment and inhibition efficiency (Rodríguez-Valdez, Martínez-Villafañe, & Glossman-Mitnik, 2005; Stoyanova, Petkova, & Peyerimhoff, 2002).

The value of $E_{\text{HOMO}}$ is higher in the case of AQ-1 than AQ-2 and AQ-3, which is due to the presence of electron donor CH$_3$ group in the molecular framework of AQ-1. So, AQ-1 has higher

### Table 5. Calculated quantum chemical parameters of non-protonated AQs

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$\mu$</th>
<th>$E_{\text{HOMO}}$</th>
<th>$E_{\text{LUMO}}$</th>
<th>$\Delta E$</th>
<th>N$_1$</th>
<th>N$_{12}$</th>
<th>N$_{23}$</th>
<th>O$_{11}$</th>
<th>O$_{21}$</th>
<th>O$_{20}$</th>
<th>O$_{22}$</th>
<th>O$_{24}$</th>
<th>O$_{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQ-1</td>
<td>5.051</td>
<td>-8.146</td>
<td>-5.983</td>
<td>2.163</td>
<td>-0.624</td>
<td>-0.223</td>
<td>-0.413</td>
<td>-0.401</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AQ-2</td>
<td>5.743</td>
<td>-8.178</td>
<td>-5.758</td>
<td>2.42</td>
<td>-0.63</td>
<td>-0.226</td>
<td>-0.416</td>
<td>-0.437</td>
<td>-0.396</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AQ-3</td>
<td>8.381</td>
<td>-10.336</td>
<td>-5.54</td>
<td>4.826</td>
<td>-0.625</td>
<td>-0.223</td>
<td>-0.117</td>
<td>-0.405</td>
<td>-0.396</td>
<td>-0.286</td>
<td>-0.286</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: All energy values are in eV.

* $\mu$ is in Debye.
electron-donating tendency. Also the value of $E_{\text{LUMO}}$ is lower in case of AQ-1, which further supports the better corrosion performance of AQ-1. The value of $\Delta E$ is lower in case of AQ-1, which further supports its more inclination to adsorb onto the N80 steel surface. This is in good agreement with the experimentally observed result.

3.4.2. Protonated AQs

In aqueous system inhibitor molecules have a tendency to undergo protonation using their lone pairs of electrons. It has been reported that these protonated species can also take part in adsorption process. So, it becomes necessary to explain the adsorption of these protonated species. In the
present case inhibitors have four heteroatoms, out of these the most negative value of Mulliken charge containing heteroatom would have the highest probability to undergo protonation (Table 5).

**Table 6. Calculated quantum chemical parameters of protonated AQs**

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$\mu^a$</th>
<th>$E_{\text{HOMO}}$</th>
<th>$E_{\text{LUMO}}$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AQ-1</td>
<td>9.142</td>
<td>−3.494</td>
<td>−2.371</td>
<td>1.123</td>
</tr>
<tr>
<td>AQ-2</td>
<td>10.254</td>
<td>−5.59</td>
<td>−3.491</td>
<td>2.099</td>
</tr>
<tr>
<td>AQ-3</td>
<td>9.665</td>
<td>−5.75</td>
<td>−2.103</td>
<td>3.647</td>
</tr>
</tbody>
</table>

Note: All energy values are in eV.

$^a\mu$ is in Debye.
The HOMO and LUMO distributions of the preferred protonation site are shown in Figure 7(a–f). Table 6 represents the quantum chemical parameters of the preferred protonated species. After comparing the quantum chemical parameter of neutral and protonated AQs (Tables 5 and 6), it could be said that the values of $\Delta E$ in both AQs are lower in protonated forms than neutral forms, which reveal that protonated species are more reactive than neutral species i.e. greater tendency toward metal interaction. Thus, the protonated form of AQs is more likely to get adsorbed onto the N80 steel surface than neutral form. This discussion also confirmed the experimentally observed adsorption phenomenon i.e. both physical and chemical.

4. Conclusions

(1) From every study (gravimetric, EIS, and Tafel polarization) it could said that AQs are good corrosion inhibitors for N80 steel in 15% HCl.

(2) Tafel polarization study shows that AQs are mixed-type inhibitors but favoring more cathodic reaction suppression.

(3) AQs obeyed the Langmuir adsorption isotherm.

(4) $\Delta G^\text{ads}$ adsorption reveals that the adsorption of AQs is both physical and chemical.

(5) SEM micrographs show that N80 steel surface protection in the presence of AQs.

(6) Quantum chemical study revealed that AQs have a tendency to get protonated, and also these protonated forms of AQs have greater interaction and adsorption capacities than the neutral forms.

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