Experimental and computational studies of imidazolium based ionic liquid 1-methyl-3-propylimidazolium iodide on mild steel corrosion in acidic solution

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Abstract
Corrosion inhibitive property of ionic liquid 1-Methyl-3-propylimidazolium iodide (MPII) on Mild Steel in 1 M H2SO4 was investigated by experimental and computational Studies. The inhibition efficiency of inhibitor MPII at various concentrations, temperature and time duration were studied by gravimetric measurements, potentiodynamic polarization techniques, electrochemical impedance spectroscopy (EIS), surface studies and computational studies. The results from potentiodynamic polarization studies revealed that inhibitor 1-Methyl-3-propylimidazolium iodide acts as a mixed type inhibitor with a high inhibition efficiency of 91% at 298 K. Adsorption of the inhibitor on the surface of mild steel follows the Langmuir adsorption isotherm. The mechanism of adsorption was also validated by quantum chemical studies. Morphology and topography of the Mild Steel surface with and without the inhibitor were investigated by SEM. Thermodynamic parameters for adsorption like adsorption equilibrium (Kads), ΔH_ads, ΔS_ads, Free energy of adsorption i.e. ΔG_ads were also calculated so as to project the mechanism of adsorption. Computational data obtained from the Density functional theory (DFT) were used to acquire detailed theoretical insights. Appreciably Electrochemical impedance spectroscopy, Molecular dynamic simulation and quantum chemical calculation confirms the interaction of inhibitor with metal which leads to increases in inhibition efficiency.

1. Introduction
Mild steel is widely inconceivably utilized in the pipelines industries, automobiles manufacture, oil and gas transportation industries due to its low tensile firmness, durability and price [1–6]. When it comes in the contact with the traces of water and salts present in the oil tanks, pipelines and with the acids which are used to remove the oxide layer and rust surface during the acid pickling, it starts getting corroded. However, this cleaned mild steel surface has been corroded by aggressive ions during the cleaning treatment itself.

To protect the corrosion of mild steel, a different type of organic inhibitors were used. However, with increasing concern about environmental pollution and human health, the application of such organic inhibitors has been limited world-wide owing to their high toxicity. Ionic liquids have attracted considerable attention in recent years due to its non-toxicity, cost effectiveness and eco-friendly nature which have framed it to be as one of the best corrosion inhibitor for mild steel and several other metals and their alloys. They have also been identified as media for green synthesis which are used in a wide range of chemical processes. Ionic liquids are described as the organic salts which are having melting points below 373 K, high thermal adherence, acute low vapour pressure, wide electrochemical window and non-ignitable properties which makes ionic liquids as...
potentially attractive alternatives for volatile organic solvents inhibitor for mild steel corrosion [7, 8]. Ionic liquids are composed of both cationic and anionic part. Cationic part is heteroatom (N,P,S) containing larger organic part such as N-alkylimidazolium, alkylammonium, alklypyridinium and alklyphosphonium whereas anionic part is inorganic containing Cl$^-$, Br$^-$, I$^-$ and have smaller size [9, 10]. Recently, some researchers proposed interpretation of the size effects of halide ions but in our case of mild steel this might not play a major role [11, 12]. Imidazolium compounds are reported to show corrosion resistant behaviour on various metals and alloys such as copper, aluminium, mild steel etc.

The present study is undertaken to investigate the inhibition effect of Imidazolium based ionic liquid 1-Methyl-3-propylimidazolium iodide (MPII) on Mild Steel treated in acid solution. Experimental data obtained from the several techniques at different temperatures is used to determine the thermodynamic functions for the adsorption process and gain more information about the corrosion inhibition behaviour and mode of adsorption of ionic liquid 1-Methyl-3-propylimidazolium iodide (MPII) on the surface of Mild Steel.

2. Material and methods

2.1. Preparation of material

Mild steel of elemental weight percentage composition with C(0.16%), Mn(0.70%), Si(0.14%), P(0.04%), Cr(0.018), S(0.055%), Mo(0.014%), Ti(0.02%), V(0.002%) and balanced Fe was cut into small pieces of dimensions 1 cm $\times$ 1 cm (L,B). Then it was rubbed with emery papers of different grades range from 100–1500 to remove the corrosive surface of the metal and later on washed with double distilled water followed by acetone and finally air dried. Gravimetric studies were performed on these mild steel pieces with an area dimension of 1 cm$^2$ each.

2.2. Acid solution preparation

The acid solution was prepared from the H$_2$SO$_4$ with maximum assay of 98%. It was diluted with double distilled water to form 1 M H$_2$SO$_4$. To avoid any type of contamination or irregularity in the acid concentration, this standard acid solution was further standardized and diluted to prepare the desired concentration.

2.3. Gravimetric studies

Weight loss or gravimetric methods were done on the coupons of mild steel with an area of 1 cm$^2$ in 1 M H$_2$SO$_4$ to determine inhibition efficiency and surface coverage of inhibitor. This study includes determination of inhibition efficiency at different concentration, time and temperature by measuring the weight loss in the mild steel with and without inhibitor in acid immersion. The corrosion rate and surface coverage were calculated by the following equations [13]:

$$C_R = \frac{(87.6^*W)}{A^*T^*D}$$

(1)

$$\theta = \frac{\eta(\%)}{100}$$

(2)

Where, $C_R$ is corrosion rate in mmppy$^{-1}$, W in weight loss in mg, A is the area of the metal coupons in cm$^2$, D is the density of the metal in gcm$^{-3}$, $\theta$ is the surface charge coverage, $\eta$ is inhibition efficiency which was calculated by using the following equation

$$\eta(\%) = \frac{C_{Ro} - C_R}{C_{Ro}} * 100$$

(3)

Where, $C_{Ro}$ and $C_R$ are the weight loss in the absence and presence of the inhibitor [14–20].

2.4. Electrochemical methods

An electrochemical study includes the polarisation and electrochemical impedance methods. These were carried out by setting the polarization cell, which includes three electrode system that were described as the working, reference and the counter electrode respectively, connected through potentiostat at room temperature [16]. Later on these cells were immersed in four distinctive water baths under various temperatures 298 K, 308 K, 318 K and 328 K to study the mild steel corrosion. At a specific time when the stable open circuit potential (OCP) was attained, the examination of impedance spectrum after OCP stabilization was done under a well maintained frequency range from $1 \times 10^3$ Hz to 1 Hz on 0.005 V amplitude value. Tafel plot was determined by polarizing the working electrode to $\pm300$ mV from $E_{op}$ at 1 mV s$^{-1}$ scan rate. The inhibition efficiency of potentiodynamic polarisation ($\eta_{PDP}$) were calculated from $i_{corr}$ values using this equation.
\[ \eta_{PD} = \left(1 - \frac{I_{corr}}{I_{corr0}}\right) \times 100 \]  
(4)

Where, \( I_{corr} \) and \( I_{corr0} \) were the corrosion current in the presence and absence of the inhibitor.

The Nyquist plot helps in the determination of polarisation resistance values which was used to find the inhibition efficiency by using the following equation

\[ \eta_{ESS} = \left(\frac{R_P(\text{inh}) - R_P}{R_P(\text{inh})}\right) \times 100 \]  
(5)

Here, \( R_P(\text{inh}) \) and \( R_P \) were the polarization resistance in the presence and absence of the inhibitor with different concentration of the inhibitor at 298 K [21–27].

### 2.5. Computational studies

Computational parameters include the detailed study of the structural geometry of the inhibitor which was studied by B3LYP methods with SV (P), SV/J level of basis set. Herein, the ORCA programme package, 2.7.0 version has been used for all DFT calculations [Ref: F. Neese, An Ab initio, DFT and Semiempirical SCF-MO Package, Version 2.7.0, Max Planck Institute for Bioinorganic Chemistry, Mulheim an der Ruhr, Germany, 2012]. Quantum calculation gives the whole energy values of HOMO and LUMO orbital’s of the inhibitor and these values of energy were used to calculate the ionisation energy and electronic affinity [1, 18].

\[ IP = -E_{\text{HOMO}} \]  
(6)

\[ EA = -E_{\text{LUMO}} \]  
(7)

To calculate the Chemical hardness (\( \chi \)) and Electronegativity (\( \eta \)) of the molecule, the following equations were used

\[ \chi = \frac{IP + EA}{2} \]  
(8)

\[ \eta = \frac{IP - EA}{2} \]  
(9)

The fraction of electron transferred to the surface of mild steel from the inhibitor was calculated by using the following equation

\[ \Delta N = \frac{\Phi - \chi_{\text{inh}}}{2(\eta_{Fe} + \eta_{\text{inh}})} \]  
(10)

Where, \( \Phi \) represents the work function and the \( \eta_{Fe} = 0 \) for Fe (110) surface.

The Fukui indices analysis were performed by Dmol3 module in Material Studio™ (Version 6.1) by using the generalised gradient approximation (GGA) and BLYP exchange-correlation functional with the co-operational setup of double numerical polarization (DNP) basis set. Fukui functions give the reactivity of the inhibitor molecule on the metal surface by using Hirshfeld population analysis. Following equation were used to calculate Fukui function values

\[ f_k^+ = q_k(N + 1) - q_k(N) \]  
\[ f_k^- = q_k(N) - q_k(N - 1) \]  
(11)

Here \( q_k(N + 1) \), \( q_k(N - 1) \), \( q_k(N) \) are anionic, cationic and neutral charges of the inhibitor molecule respectively [28].

MD simulations were performed using discover module Material Studio software 6.1 (from Accelrys Inc.) to model the adsorption behaviour of the inhibitor molecules onto the Fe (110) surface. Molecular dynamic simulation studies were carried out with CVFF force field over 10 layers of Fe using a canonical ensemble (NVT) with a total simulation time period of 200 ps and the time step of 1.00 fs in simulation box of size (39.859 \* 39.859 \* 77.144) \( \text{Å}^3 \) at 298 K temperature. To resemble the experimental condition, along with the inhibitor molecule \( \text{H}_2\text{O}, \text{H}_3\text{O}^+, \text{SO}_4^{2-} \) ions are also considered. The molecular dynamic simulation gives interaction and binding energies of the studied inhibitor molecules. These were calculated by using the following equations [29, 30]

\[ E_{interaction} = E_{\text{total}} - (E_{\text{surface} + \text{solution}} + E_{\text{inhibitor}}) \]  
(13)

\[ E_{\text{binding}} = -E_{\text{interaction}} \]  
(14)

Where \( E_{\text{total}} \) gives the overall energy of the whole system, \( E_{\text{surface} + \text{solution}} + E_{\text{inhibitor}} \) gives the total energy of Fe (110) on the surface of the metal with acid solution and \( E_{\text{inhibitor}} \) gives the value of total energy of the inhibitor.
3. Result and discussion

3.1. Gravimetric studies
Gravimetric studies or weight loss studies were carried out in order to determine the inhibition efficiency of inhibitor and its surface coverage on the surface of mild steel with changes in the concentration of the inhibitor, immersion time and the temperature. The result showed that with an increase in the concentration of the inhibitor, inhibitor efficiency increases and whereas with an increase in the immersion time and temperature, the inhibitor efficiency decreases. The corrosion rate is inversely proportional to the concentration of inhibitor whereas surface coverage is directly proportional to the concentration of inhibitor [31, 32]. Figures 1–3 and tables 1–3 shows all the result of gravimetric studies respectively.

3.2. Electrochemical impedance studies
Results drawn from electrochemical impedance spectroscopy with respect to the inhibitor concentration at 298 K were depicted graphically in figure 4 as Nyquist plots. The main phenomenon behind the analysis was termed out to be charge transfer because there was a depiction of semi circular impedance spectra. Nyquist plot
demonstrates that with an increase in the concentration of the inhibitor MPII, the diameter of the capacitive loop increases. This study confirms the formation of a protective layer of the inhibitor over the surface of mild steel which prevents the corrosion of mild steel \[33–39\]. Data obtained from the EIS are tabulated in table 4.

Table 1. Effect of concentration of MPII on the corrosion inhibition of mild steel in 1 M H\(_2\)SO\(_4\).

| Concentration (ppm) | Initial weight (mg) | Final weight (mg) | Weight Loss (mg) | \(\eta(\%)\) |
|---------------------|---------------------|-------------------|-----------------|-------------|
| 100                 | 10.445              | 10.385            | 0.574           | 54.142      |
| 250                 | 10.883              | 10.890            | 0.395           | 68.458      |
| 500                 | 10.730              | 10.704            | 0.242           | 80.656      |
| 1000                | 11.105              | 10.930            | 0.108           | 91.373      |

Table 2. Effect of temperature on the corrosion inhibition of mild steel by MPII at 1000 ppm in 1 M H\(_2\)SO\(_4\).

| Temp(K) | Initial \((I)\) (mg) | Final \((F)\) (mg) | Weight loss (mg) | \(\eta(\%)\) |
|---------|----------------------|-------------------|-----------------|-------------|
| 298 K   | 13.031               | 13.017            | 0.107           | 91.453      |
| 308 K   | 12.862               | 12.837            | 0.194           | 86.771      |
| 318 K   | 10.645               | 10.567            | 0.732           | 77.788      |

Table 3. Effect of time on the corrosion inhibition of mild steel by MPII at 1000 ppm in 1 M H\(_2\)SO\(_4\).

| Time (Hours) | Initial \((I)\) (mg) | Final \((F)\) (mg) | Weight loss (mg) | \(\eta(\%)\) |
|--------------|----------------------|-------------------|-----------------|-------------|
| 1            | 11.056               | 11.052            | 0.036           | 91.524      |
| 2            | 11.404               | 11.394            | 0.087           | 92.964      |
| 3            | 10.464               | 10.426            | 0.363           | 75.850      |
| 4            | 11.304               | 11.222            | 0.725           | 63.222      |
| 5            | 12.065               | 11.925            | 1.160           | 56.352      |

Figure 3. Efficiency versus Time graph showing variation of Inhibition efficiency of MPII with time in 1 M H\(_2\)SO\(_4\).
3.3. Potentiodynamic polarization studies

Potentiodynamic polarization studies were conducted for the dissolution process of mild steel in acidic medium at a temperature range of 298–328 K under several concentrations of inhibitor represented in figure 5. Figure 5 shows the Tafel plot of Potentiodynamic polarization, in addition the curves of anodic site moved toward the amassed positive potentials while in case of cathodic curves it moved toward the amassed negative potentials, prompting the decrease in rate of corrosion current densities.

Table 4. EIS data for the corrosion of mild steel in 1 M H₂SO₄ using MPII as inhibitor at different concentration at temperature 298 K.

| Inhibitor Concentration(ppm) | Rp(inh) | Rp(blank) | η_{EIS} (%) | C_{Blank}(μF) | C_{Inhibitor}(μF) |
|-----------------------------|--------|----------|-------------|--------------|------------------|
| 100                         | 30.781 | 14.116   | 54.100      | 2165.580     | 296.620          |
| 250                         | 44.716 | 14.116   | 68.460      | 2165.580     | 247.980          |
| 500                         | 72.973 | 14.116   | 80.670      | 2165.580     | 183.210          |
| 1000                        | 163.379| 14.116   | 91.730      | 2165.580     | 99.790           |
Whereas Table 5 gives the value of corrosion current density ($I_{corr}$) of blank as also in the presence of inhibitor MPII, cathodic and anodic slopes ($\beta_c$ and $\beta_a$), and inhibition efficiency. The decrease in the $I_{corr}$ value of inhibitor with an increase in the concentration of inhibitor can be clearly observed in the polarization curve. In the anodic polarization, potential shifts towards the more positive value while in the case of cathodic polarization, potential shifts towards the negative value which shows that the inhibitor is a mixed type inhibitor. From which it can be anticipated that the inhibition of corrosion on the mild steel takes place by inhibiting the active site of corrosion [40–50].

### 3.4. Adsorption studies

The adsorption studies value of $\Delta G_{\text{ads}}$ and $K_{\text{ads}}$ for the interaction between metal and inhibitor were obtained as shown in Table 6. Figure 6 represents a straight line in the graph between $C$ versus $C/\theta$ with the regression coefficient ($R^2$) nearly equals to 1 which shows that Langmuir adsorption isotherm [13,51–54] was being obeyed.

The following equations were used in the adsorption studies

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C$$  \hspace{1cm} (15)

Where, $\theta$ and $K_{\text{ads}}$ was concentration of inhibitor, surface coverage and adsorption equilibrium respectively. From this it can be concluded that monolayer was formed at the surface of a metal by inhibitor MPII [55–58].

**Figure 6.** Plot for Langmuir adsorption isotherm for MPII in 1 M H$_2$SO$_4$ adsorbed on the surface of mild steel.

| Inhibitor concentration (ppm) | $I_{corr}$ (mA cm$^{-2}$) | $I_{corr}^0$ (mA cm$^{-2}$) | $\beta_a$ (mV dec$^{-1}$) | $\beta_c$ (mV dec$^{-1}$) | $E_{corr}$ (mV) | $\eta_{ip}$ (%) |
|-------------------------------|--------------------------|-----------------------------|--------------------------|--------------------------|----------------|----------------|
| Blank                         | 7.876                    | 274.273                     | 171.556                  | 475                      | —              | 100            |
| 100                           | 7.876                    | 3.622                       | 132.90                   | 118.807                  | 432            | 54.321         |
| 250                           | 7.876                    | 2.484                       | 146.563                  | 131.682                  | 439            | 68.485         |
| 500                           | 7.876                    | 1.523                       | 97.541                   | 101.978                  | 600            | 80.450         |
| 1000                          | 7.876                    | 0.679                       | 104.220                  | 101.214                  | 488            | 91.327         |

**Table 5.** Tafel polarization data for corrosion of mild steel in 1 M H$_2$SO$_4$ with different concentration of MPII.

| Temperature (K) | log $K_{\text{ads}}$ (M$^{-1}$) | $\Delta G_{\text{ads}}$ (KJ mol$^{-1}$) |
|-----------------|---------------------------------|----------------------------------------|
| 298             | 35.136                          | −18.772                                |

**Table 6.** Equilibrium constant and Gibbs free energy parameters of MPII as an effective corrosion inhibitor for Mild steel at 298 K.

Whereas table 5 gives the value of corrosion current density ($I_{corr}$) of blank as also in the presence of inhibitor MPII, cathodic and anodic slopes ($\beta_c$ and $\beta_a$), and inhibition efficiency. The decrease in the $I_{corr}$ value of inhibitor with an increase in the concentration of inhibitor can be clearly observed in the polarization curve. In the anodic polarization, potential shift towards the more positive value while in the case of cathodic polarization, potential shifts towards the negative value which shows that the inhibitor is a mixed type inhibitor. From which it can be anticipated that the inhibition of corrosion on the mild steel takes place by inhibiting the active site of corrosion [40–50].
Gibbs free energy was also calculated from the value of $K_{ads}$ by using the following equation

$$\Delta G_{ads} = -RT \ln(K_{ads}) \tag{16}$$

Here, $\Delta G_{ads}$, R and T are the Gibbs free energy adsorption, gas constant and temperature respectively and the molar concentration of water was 55.5. The negative value of $\Delta G_{ads}$ reveals that the adsorption was spontaneous and electrostatic physical in nature [55, 56, 59, 60].

3.5. Thermodynamic parameters

In order to study the thermodynamic parameters, rate of corrosion was studied between 298–318 K. The activation energy ($E_a$) was calculated by the following equation

$$\log C_R = -\frac{E_a}{2.303RT} + \log A \tag{17}$$

Here $C_R$, $E_a$, R, T and A are corrosion rate, activation energy, gas constant, temperature and Arrhenius constant respectively. The graph shown in figure 7 between log $C_R$ VS 1/T forms a straight line. From the slope $\frac{E_a}{2.303RT}$ value of $E_a$ was found. The result showed that the value of $E_a$ with the inhibitor is more than in the case of without inhibitor, which confirms the formation of a protective layer over the mild steel surface [61, 62]. The value of enthalpy was determined by using the Eyring equation [63] which is given below

$$\log \frac{C_R}{T} = \log \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S}{2.303R} \right) + \left( \frac{-\Delta H}{2.303RT} \right) \tag{18}$$

Here N, $\Delta S$, $\Delta H$, and h are Avogadro number, Adsorption entropy, Adsorption enthalpy and Plank constant respectively. The Graph between $\log \frac{C_R}{T}$ versus 1/T is shown in figure 8 and from the slope $\frac{-\Delta H}{2.303RT}$ value, $\Delta H$ was calculated. Whereas $\Delta S$ was calculated from the following equation

$$\Delta S_{ads} = (\Delta H_{ads}^0 - \Delta G_{ads}^0) \tag{19}$$

Table 7 shows all the thermodynamic parameters values in the presence and absence of the inhibitor. The dissolution of the mild steel in the solution was observed as endothermic in nature, as confirmed by the positive value of enthalpy. In the presence of inhibitor MPII the entropy value increases which was the driving force for the adsorption of the inhibitor on the metal surface. The positive value of entropy termed out to be the process function of substitution which was supposed to be due to desorption of water. Thus it can be concluded that the increase in entropy value was due to the desorption of water from the metal surface [64].

3.6. FTIR analysis

The observed peaks of 1-methyl-3-propylimidazoliumiodide MPII was as N-H peak at 3443 cm$^{-1}$, –CH$_3$ at 1460 cm$^{-1}$, 2870 cm$^{-1}$, 2958 cm$^{-1}$ show the alkyl chain peaks of symmetric and asymmetric stretching. Whereas the C–H stretching of imidazolium ring were shown in 3146 cm$^{-1}$, 3088 cm$^{-1}$. Remaining peaks were also observed like 1022 cm$^{-1}$ for S–O, 1338 cm$^{-1}$ for S–OH of H$_2$SO$_4$, 1166 cm$^{-1}$ show C–N stretching, 831 cm$^{-1}$ show C–H stretching in bending plane vibration of Imidazolium iodide, 750 cm$^{-1}$ shows C–H stretching out of plane bending in imidazolium ring. There was no change in the peaks of aliphatic alkyl chains.
which represents that they were not responsible for the adsorption process. A peak at 1622 cm$^{-1}$ shows the interaction of Fe with N of ionic liquid. The Disappearance of C–N peak at 1020 cm$^{-1}$ was observed in the pure ionic liquid sample which shows the involvement of N heteroatom of the ionic liquid in the adsorption process on mild steel. IR spectra of pure ionic liquid and its interaction with mild steel respectively are being shown in figures 9 and 10 [65, 66].

3.7. UV analysis

The UV analysis was done with the help of SHIMADZU1800 instrument. UV Spectrum of inhibitor MPII at 1000 ppm in 1 M H$_2$SO$_4$ and inhibitor MPII at the same concentration after interaction with mild steel is shown in figure 8.

| Inhibitor            | $E_a$ (KJmol$^{-1}$) | $\Delta S_{ad}$ (KJ mol$^{-1}$) | $\Delta H$ (KJmol$^{-1}$) |
|----------------------|----------------------|---------------------------------|-----------------------------|
| Blank                | $-1.285$             | $-$                             | $-7.132$                    |
| MPII (1000 ppm)      | $22.440$             | $0.309$                         | $73.348$                    |

Table 7. Adsorption, kinetic and thermodynamic parameters of MPII as an effective corrosion inhibitor for Mild steel.

![Figure 8. Transition state plot determining the values of enthalpy.](image8.png)

![Figure 9. IR of inhibitor MPII in pure form.](image9.png)
3.8. Surface studies
Surface morphological studies were done by using SEM instrument analysis. Three samples of mild steel were analysed in which one was in the pure form, the second was immersed in 1 M H₂SO₄ and the third sample was immersed in acid with inhibitor MPII [41, 68–72]. The SEM images clearly indicates the surface of mild steel with inhibitor was smooth as compared with the other two mild steel samples in pure form and immersed in 1 M H₂SO₄ which confirms the formation of an inhibitive layer on the surface of mild steel [73, 74]. Results of SEM (Scanning Electron Microscope) were shown in figure 12 [33].

3.9. Quantum chemical studies
The electron donation and acceptation between the inhibitor and metal during corrosion inhibition were studied by Quantum chemical calculation by utilising the Density functional theory. Some of the researchers have done the ab initio computation studies of passive film properties on copper [75]. It gives the details about the sites and efficiency of adsorption taking place between metal and the inhibitor. The activity of inhibitor molecule was analysed through the structure of frontier orbitals that were HOMO (Highest Occupied Molecular
Orbital and LUMO (Lowest Unoccupied Molecular Orbital) [76–78]. The distribution of electron density structure i.e. HOMO and LUMO of inhibitor were shown in figure 13. Where the HOMO distribution of electrons over the inhibitor shows the participation of inhibitor in the donation of the electron to the vacant Fe orbital of the metal surface which results in the corrosion inhibition of the metal by forming a coordinate bond through heteroatom of inhibitor. On the other side, LUMO distribution of electrons over the inhibitor molecules shows that it can accept the electrons from the Fe orbital of metal and hence shows the donor acceptance behaviour which leads to the formation of protective layer over the metal surface [28, 79].

Quantum chemical parameters shown in table 8 and 9. The higher value of $E_{\text{HOMO}}$ represents the higher donation of electrons whereas lower values of $E_{\text{LUMO}}$ represents higher chances of electron acceptance. The reactivity of inhibitor was determined by the $\Delta E$ ($E_{\text{HOMO}} - E_{\text{LUMO}}$), high value of $\Delta E$ represents high reactivity of inhibitor molecule with metal that results in increase in inhibition efficiency. Another parameter is $\Delta N$ that is number of electron transferred during the metal inhibitor interaction. The higher value of $\Delta N$ gives the efficient rate of adsorption of inhibitor over the metal surface which results in higher inhibition efficiency [29, 30, 80, 81].

### Table 8. Quantum chemical parameters of MPII using chemical package MOPAC 6.0 of Hyperchem 7.5.

| Inhibitor      | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $\Delta E$ (eV) | $\mu$ (Debye) | $I = -E_{\text{HOMO}}$ | $A = -E_{\text{LUMO}}$ | $\chi$ | $H$ | $S$ | $\Delta N_{1\text{H}}$ |
|----------------|------------------------|------------------------|-----------------|--------------|------------------------|------------------------|-------|-----|----|----------------------|
| Ionic liquid   | -7.662                 | -0.795                 | 6.866           | 4.097        | 7.662                  | 0.795                  | 4.228 | 3.433 | 0.291 | 0.086                |

Figure 12. SEM images of (a) Mild steel (b) Mild Steel + Acid (c) Mild Steel + Acid + MPII (1000ppm) in 1 M H$_2$SO$_4$.

Figure 13. Optimized structures of HOMO and LUMO of ionic liquid 1-Methyl-3-propylimidazolium iodide (MPII).
Fukui functions provide the local reactivity properties, it gives the atomic sites present inside the inhibitor molecule for reactivity. $f_k^+$ measures change in the density when molecule receive electrons and it corresponds with nucleophilic attack while $f_k^-$ measures the change in density when molecule donate electrons and it corresponds with electrophilic attack. The capacity of inhibitor molecule to get polarised on application of external electric field were also determined by Fukui functions. The highest value $f_k^+$ gives the preferred sites for nucleophilic attack while $f_k^-$ highest value gives preferred site for electrophilic attack. Table 9 represents the

Table 9. Fukui functions for the atomic sites of inhibitor (MPII).

| Atoms | Inhibitor | $f_k^-$ | $f_k^+$ |
|-------|-----------|---------|---------|
| N (1)  | 0.097     | 0.090   |
| C(2)   | 0.204     | 0.239   |
| C(3)   | 0.087     | 0.075   |
| C(4)   | 0.076     | 0.063   |
| N (5)  | 0.087     | 0.078   |
| C(6)   | 0.020     | 0.020   |
| C(7)   | 0.034     | 0.036   |
| C(8)   | 0.012     | 0.012   |
| C(9)   | 0.008     | 0.007   |

Fukui functions provides the local reactivity properties, it gives the atomic sites present inside the inhibitor molecule for reactivity. $f_k^+$ measures change in the density when molecule receive electrons and it corresponds with nucleophilic attack while $f_k^-$ measures the change in density when molecule donate electrons and it corresponds with electrophilic attack. The capacity of inhibitor molecule to get polarised on application of external electric field were also determined by Fukui functions. The highest value $f_k^+$ gives the preferred sites for nucleophilic attack while $f_k^-$ highest value gives preferred site for electrophilic attack. Table 9 represents the

Figure 14. Equilibrium adsorption configuration of the inhibitor on the Fe (110) surface at 298 K obtained from MD simulations. Left: side view, Right: top view.

Figure 15. Temperature and energy variation curves obtained from MD simulations for inhibitor (MPII) at 298 K.
values of Fukui functions. The result shows that the reactive sites were heteroatom and π-electrons of inhibitor molecule that inhibits the metal corrosion [29].

3.10. Molecular dynamic simulation studies

Through Molecular Dynamic Studies, the experimental conditions of the interaction of inhibitor and mild steel were carried out. Figure 14 represents the Equilibrium adsorption of inhibitor on Fe (110) surface at 298 K temperature. Results showed that the inhibitor molecules which were adsorbed on the metal surface closely related to a flat configuration. Flat configuration enhanced the coverage of inhibitor over corrosion active site of metal which leads to inhibition of corrosion. Parameters of the molecular dynamic simulation are represented in table 10. A high negative value of $E_{\text{interaction}}$ shows the greater binding of inhibitor with metal and leads to a higher value of $E_{\text{binding}}$ which results in greater inhibition efficiency. Figure 15 represents the temperature and energy variation obtained from molecular dynamic simulation for inhibitor at 298 K temperature [28–30, 79, 80].

4. Conclusion

MPII act as a potential mild steel corrosion inhibitor in acidic medium as suggested by the results showing 91% inhibition efficiency at 1000 ppm concentration. The inhibitor concentration was legitimately impacting the corrosion inhibition efficiency while as higher temperatures lower the inhibition efficiency. From electrochemical studies and Tafel plot, it can be concluded that the inhibitor shows mixed type behaviour that inhibits both cathodic and anodic type of chemical processes in order to inhibit corrosion by forming a thin protective layer on the mild steel surface. A surface morphological study confirms that the surface of mild is shielded by an inhibitor which blocks the active site of corrosion of the metal. The adsorption of the inhibitor over the surface of mild steel tends to follow Langmuir adsorption isotherm and a high value of adsorption equilibrium ($K_{\text{ad}}$) shows that adsorption took place is strong and attractive [75–78, 87]. From the DFT and Quantum chemical calculation, the mechanism of inhibition can be well understood. The interaction between mild steel and inhibitor as well as the configuration of adsorption is further confirmed through molecular dynamic simulation and thereby inhibits corrosion on the surface of mild steel [28–30, 80, 81]. MPII showed comparable inhibition efficiency as compared to some other studied ionic liquids such as 1-ethyl-3-methylimidazolium chloride (EMIm Cl) [82], 1-octyl-3-methyl imidazolium chloride [83], 3-(4-ethoxy-4-oxobutyl)-1-ethylimidazol-3-ium bromide [84], 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulphate [85] and N,N-dimethyl-N-dodecyl-Nethyl-ammonium ethyl sulfate [86] having almost same order of inhibition efficiencies for corrosion inhibition for mild steel.

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