# CORROSION INHIBITION EFFICIENCY OF IMIDAZOLIUM-BASED INHIBITOR FOR MILD STEEL IN 0.5 M $H_2SO_4$ MEDIUM

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## Abstract

The work carried out in this paper was specially designed to determine the efficiency of the imidazolium-based inhibitor to inhibit the corrosion of mild steel in a sulfuric acid solution. This was 1-Ethyl-3-methylimidazolium chloride [EMIM]Cl of which the concentration varied in $10^{-2}$, $10^{-3}$, $10^{-4}$, and $10^{-5}$ M and the solution was prepared with 0.5M $H_2SO_4$ and mild steel as the sample. From the results of the weight loss measurements, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and it also became clear that the performance of the steel increased in the presence of the inhibitor when immersed in various temperatures. Various Tafel plots prepared for the investigation unraveled the nature of ionic liquid that it was a mixed inhibitor inhibiting both anodic metal dissolution as well as cathodic events. In the EIS analysis, Inhibition efficiency was 94.51 % at the optimum concentration of $10^{-2}$ M. This was agreed by the results obtained from SEM and AFM imaging which provided evidence of the formation of a protective layer. It was however noted that the inhibition efficiencies were comparatively higher when the temperatures were low and this indicates that the formation of the inhibitive film is through the adsorption mechanism.

**Keywords:** Mild steel, weight loss, electrochemical studies, SEM, AFM

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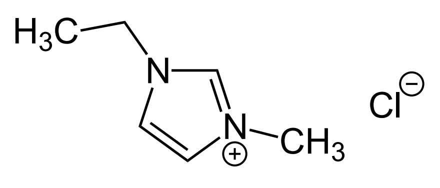
## 1. Introduction

Mild steel is favored in various manufacturing because of its low production costs & favorable mechanical properties [1]. Acidic solutions find extensive use in manufacturing procedures such as oil well acidizing, metal pickling, and cleaning. To mitigate corrosion, inhibitors are commonly applied [2- 4]. Organic compounds, featuring heteroatoms like S, O, P, and N along with π electron systems, serve as corrosion inhibitors by adsorbing onto metal surfaces. This adsorption can occur via covalent bond formation (chemisorption) or electrostatic interaction (physisorption). Therefore, efforts have been directed towards developing affordable organic inhibitors [5-8].

This research proposes to evaluate the inhibitory effectiveness of the investigated inhibitor for mild steel in a 0.5M sulfuric acid ($H_2SO_4$) solution through electrochemical analysis and weight loss experiments. Surface morphology was examined using SEM and AFM techniques. 1-Ethyl-3-methylimidazolium chloride [EMIM]Cl serves as the inhibitor in this study. Organic compounds have garnered attention for their ability to form protective layers on metal surfaces, attributed to heteroatoms like sulfur (S), oxygen (O), phosphorus (P), and nitrogen (N), in addition to π electron systems. Consequently, there is a collective effort in the scientific community to develop novel and cost-effective organic inhibitors capable of effectively delaying corrosion processes, thus extending the lifespan of metal assets [6]. The chemical properties and molecular structures of inhibitors are depicted in Table 1.

**Table 1**: Inhibitors used for the present study are discussed in detail with their respective properties, names and structures below:

| **1-Ethyl-3-methylimidazolium chloride [EMIM]Cl** | |  |
|---|---|---|
| Molecular Formula | $C_6H_{11}ClN_2$ | |
| Molecular Weight | 146.62 g/mol | |
| Assay | 98 % | |
| Melting Point | 79 ºC | |
| Physical State | Solid | |
| Solubility in Water | Soluble | |

## 2. Experimental Procedure

Table 2 illustrates the composition of the mild steel utilized for preparing coupons in this study.

**Table 2:** Mild steel composition

| **Element** | C | Si | S | Mn | Fe |
|---|---|---|---|---|---|
| **Weight (%)** | 0.15 | 0.08 | 0.02 | 1.02 | 98.72 |

### 2.1 Weight loss measurements

To evaluate weight loss, mild steel coupons sized 1×1×1 cm (Length × Breadth × Height) were employed to assess the corrosion inhibition potential of the inhibitor. These coupons were immersed in 100 mL of 0.5 M $H_2SO_4$ for 6 hours at 25°C, with varying inhibitor concentrations ($10^{-2}$ M, $10^{-3}$ M, $10^{-4}$ M, and $10^{-5}$ M). Weight differences before and after immersion were measured using a Mettler Toledo analytical weighing machine.

### 2.2 Electrochemical measurements:

Electrochemical measurements were conducted using a CH electrochemical workstation (Model: CHI-760) equipped with a corrosion cell kit, utilizing a three-electrode configuration: a platinum counter electrode, a mild steel working electrode, and a saturated reference electrode. Experiments were performed in a 0.5 M $H_2SO_4$ solution at 25°C. Mild steel specimens, embedded in epoxy resin to expose a $1cm^2$ working area, were subjected to immersion for one hour. Electrode potential measurements were taken against a saturated calomel electrode (SCE), and polarization curves were recorded at a scanning rate of 1 mV/s starting from the open circuit potential (OCP). Potentiodynamic polarization studies were conducted after one hour of immersion, with curves scanned at 1 mV/s from -250 mV to +250 mV relative to the SCE. Inhibition efficiency was determined at 298K using both methods.

### 2.3 Surface characterization

Surface morphology analysis involved mild steel coupons with dimensions of 1 cm×1 cm×2 mm immersed in 0.5 M $H_2SO_4$ with and without the inhibitor for 6 hours. After removal from the solutions, samples were air-dried. SEM images were obtained using a Jeol Japan instrument (Model No. JSM-6610LV) to analyze surface roughness and topographical changes induced by corrosion and inhibitors. Comparison of inhibited and uninhibited samples demonstrated inhibitor effectiveness. Surface morphology was further examined using three-dimensional microscopic images captured with an AFM instrument (AG Nanosurf Naio AFM, Switzerland)."

## 3. Results and Discussion

### 3.1Measurements for weight loss

Table 3 lists the obtained considerations from weight loss dimensions, "such as corrosion rate (CR) and corrosion inhibition efficiency (η%)". As the concentration of inhibitor rises, mild steel corrodes at a slower rate (g $cm^{-2}$ $h^{-1}$) Fig. 1 illustrates Table 3 findings, which indicate that as inhibitor concentrations rise, inhibition efficiency also increases.

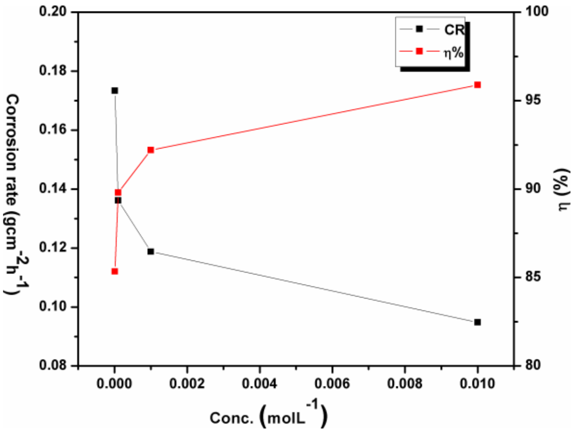


**Fig.1** Illustrates the impact of inhibitor concentrations on corrosion rate and inhibition effectiveness for mild steel (MS) in a 0.5 M $H_2SO_4$ solution at 25°C.

The equations (1) and (2) were used to find out the "inhibition efficiency" ($\eta_{WLM}$, in %) [9]

$$\eta_{WLM}\ (IE\%) = \frac{C.R._{acid} - C.R._{inh.}}{C.R._{acid}} \times 100 \qquad (1)$$

Where, C.R. = "Corrosion Rate", given by the formula:

$$C.R.\,(acid\ or\ inh.) = \frac{W_{initial} - W_{final}}{S \times t} \qquad (2)$$

Where, $W_{initial}$ = "weight (g) of plain polished coupons"
$Wf_{inal}$ = "weight (g) of the MS coupons after 6 hours of immersion"
S = "Surface area of the Mild Steel coupon ($cm^2$)"
T = "Time (h)"

**Table 3:** Corrosion parameters of mild steel in 0.5 M $H_2SO_4$ with varying concentrations of [EMIM]Cl, compared to its performance without the inhibitor, over a 6-hour duration at 25°C.

| **Conc. Molarity** | **C.R. (grams per square centimeter per hour)** | **$\eta_{WLM}$ (%)** | **θ** |
|---|---|---|---|
| $10^{-2}$ | 0.029 | 95.85 | 0.9585 |
| $10^{-3}$ | 0.054 | 92.28 | 0.9228 |
| $10^{-4}$ | 0.072 | 89.71 | 0.8971 |
| $10^{-5}$ | 0.099 | 85.85 | 0.8585 |
| 0.5M $H_2SO_4$ | 0.700 | -- | -- |

At 25°C, [EMIM]Cl concentrations were maintained for 6 hours, facilitating their adsorption onto the mild steel surface and the formation of protective layers, which effectively shield against corrosion. This protective mechanism correlates with the increased inhibition efficiency and the higher adsorption of inhibitor molecules on the mild steel surface [10].

### 3.2 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was employed to analyze Nyquist plots of mild steel immersed in 0.5 M $H_2SO_4$ solutions through varying [EMIM]Cl conc. at 25°C (Fig. 2). Following one hour of immersion to achieve steady-state potential, impedance parameters were assessed. Table 4 summarizes the results. The observed increase in the width of the capacitive loop from $10^{-5}$M to $10^{-2}$M [EMIM]Cl concentrations suggests enhanced inhibition of mild steel corrosion. According to previous studies [11–12], the semicircle depression in the plots is commonly associated with mild steel surface roughness, solid surface heterogeneity, and inhibitor adsorption.

**Table 4:** EIS Analysis of MS in 0.5M $H_2SO_4$ Solution with various concentrations of [EMIM]Cl at 298K

| **Conc. (Molarity)** | **$R_{ct}$ (ohm-centimeter squared)** | **$f_{max}$ (Hertz)** | **$C_{dl}$ (double-layer capacitance per square centimeter)** | **$\eta_{EIS}$ (%)** |
|---|---|---|---|---|
| $10^{-2}$ | 19.309 | 5.885 | 1418.21 | 94.51 |
| $10^{-3}$ | 6.756 | 2.319 | 10633.77 | 83.39 |
| $10^{-4}$ | 4.593 | 1.274 | 28457.59 | 75.67 |
| $10^{-5}$ | 2.790 | 0.807 | 71022.72 | 61.53 |
| 0.5M $H_2SO_4$ | 1.066 | 0.223 | 671140.93 | -- |

The efficiency of inhibition based on the impedance study was determined using the formula as referenced [13].

$$\mathrm{IE}(\%) = \frac{R_{ct}-R^0_{ct}}{R_{ct}} \times 100 \qquad (3)$$

The charge transfer resistance with and deprived of the inhibitor is denoted by $R_{ct}$ and $R^0_{ct}$ respectively.

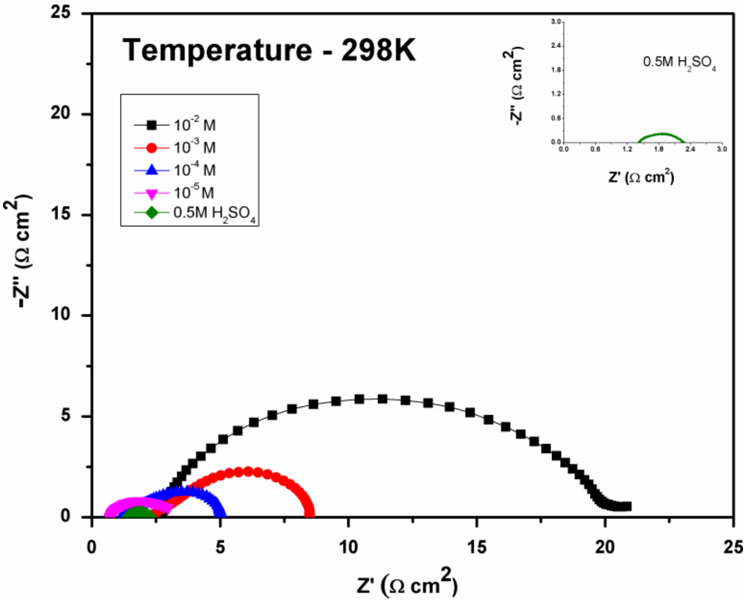


**Fig. 2** Nyquist Plots of Mild Steel in 0.5M $H_2SO_4$ Solution at 298K with Varied Inhibitor Concentrations

The results illustrate a notable increase in the values of $R_{ct}$ with the addition of [EMIM]Cl, particularly evident at the $10^{-2}$M inhibitor concentration, where the inhibition efficiency reached 94.51%. This enhancement suggests a substantial reduction in the corrosion rate due to the inhibitor's presence. Additionally, the reduction in double-layer capacitance signifies a thicker double-layer formation accredited to the adherence of inhibitor molecules to the MS surface. This phenomenon further corroborates the inhibitive properties of [EMIM]Cl on corrosion.

The following relation is also used to determine "double-layer capacitance" ($C_{dl}$)

$$C_{dl} = \frac{1}{2\pi f_{max} \cdot R_{ct}} \qquad (4)$$

The maximum frequency in the “Nyquist plot” is denoted by $f_{max}$, while the charge transfer resistance is represented by $R_{ct}$.

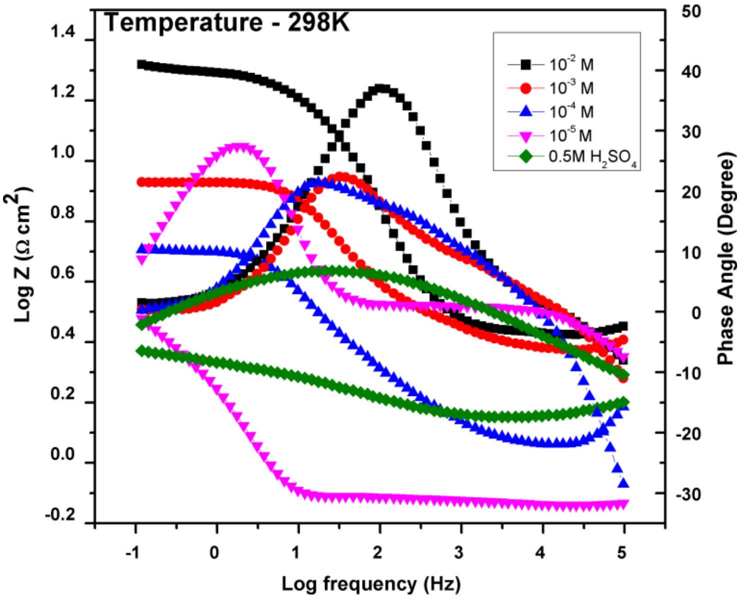


**Fig. 3** “Bode Plot (Log Z vs. Log Frequency)” and “Phase Angle Plot” of Mild Steel in 0.5M $H_2SO_4$ Solution at 298K with different Inhibitor Concentrations

It has been noted that when inhibitor concentrations rise, so increases the value of impedance. When phase angle values reach −90° and slope values reach −1, a perfect capacitor behaviour would be achieved (as noted in fig.3) [14]. The introduction of the investigated inhibitor on the mild steel surface leads to a reduction in the corrosion rate after forming a protective layer.

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### 3.3 Potentiodynamic polarization measurements

Fig. 4 depicts the “potentiodynamic polarization” curves for various inhibitor concentrations. Table 5 lists the parameters derived from polarization curves, “including inhibition efficiency (η%), cathodic and anodic Tafel slopes (βc and βa), corrosion potential ($E_{corr}$), and corrosion current density ($i_{corr}$)”.

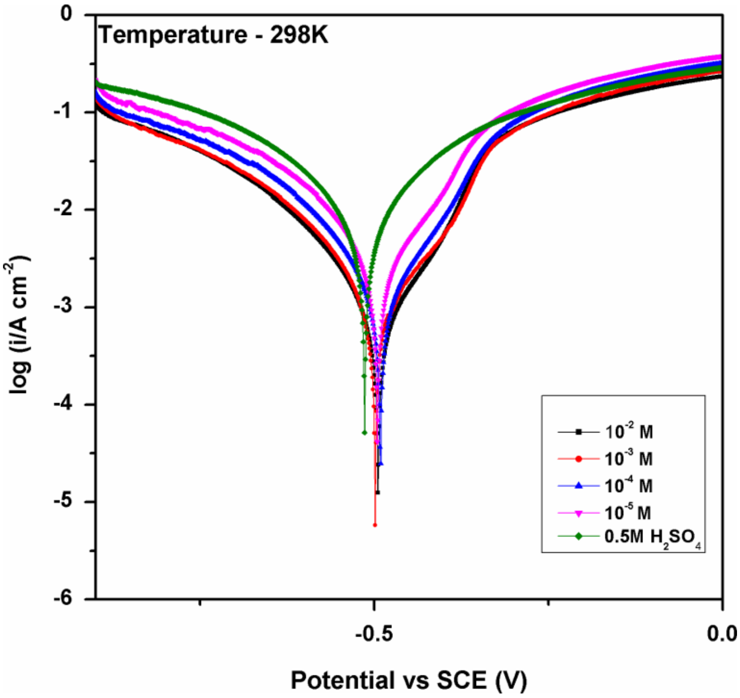

**Fig.4** MS polarization curves in 0.5M $H_2SO_4$ with and without various inhibitor concentrations at 298K.

To assess the inhibition efficiencies, the following formula was used [15]:

$$\text{Inhibition efficiency}(\eta)\% = \frac{i_{0corr} - i_{icorr}}{i_{0corr}} \times 100 \quad (5)$$

“In a 0.5M $H_2SO_4$ solution, the values of the corrosion current density for MS in the absence and presence of an inhibitor are denoted by the variables $i_{0corr}$ and $i_{icorr}$ respectively.”

**Table 5:** Mild steel polarization parameters in 0.5M $H_2SO_4$ with and without [EMIM]Cl concentrations at 298K.

| **Concentration (Molarity)** | **-$E_{corr}$ (millivolt vs. saturated calomel electrode)** | **-$\beta_c$ (millivolt per decade)** | **$\beta_a$ (millivolt per decade)** | **$I_{corr}$ (mA per centimeter square)** | **η (% )** |
|---|---|---|---|---|---|
| $10^{-2}$ | 495 | 127.40 | 80.12 | 0.789 | 90.52 |
| $10^{-3}$ | 499 | 132.97 | 106.21 | 1.197 | 85.64 |
| $10^{-4}$ | 491 | 132.10 | 89.42 | 1.445 | 82.66 |
| $10^{-5}$ | 496 | 137.19 | 90.62 | 2.606 | 68.73 |
| 0.5M $H_2SO_4$ | 514 | 155.11 | 154.70 | 8.336 | -- |

According to previous research findings, the inhibitor's functionality as either a cathodic or anodic inhibitor depends on whether the $E_{corr}$ exceeds 85 mV relative to the $E_{corr}$ values of the blank solution. Conversely, it assumes a mixed-type role if the $E_{corr}$ falls below 85 mV [16-19]. Table 5 analysis reveals that the shift in $E_{corr}$ value remains below 85 mV, indicating the investigated inhibitor, [EMIM]Cl, operates as a mixed-type inhibitor.

At 298K, inhibition efficiencies of 90.52%, 85.64%, 82.66%, and 68.73% were observed. These outcomes underscore the correlation between decreasing $i_{corr}$ values and rising corrosion inhibition efficiencies, emphasizing the protective mechanism attributed to the adsorption of [EMIM]Cl, which effectively mitigates the corrosion rate.

## 3.4 Morphological studies

### 3.4.1 SEM (scanning electron microscopy)

SEM offers comparative insights into the surface characteristics before and after the addition of [EMIM]Cl inhibitor. The SEM pictures depicted in Fig. 5(a) show a polished MS surface, serving as a baseline for comparison. In contrast, Fig. 5(b) exhibits a highly damaged and roughened surface, indicative of corrosion induced by the acidic environment of the 0.5M $H_2SO_4$ solution. Notably, Fig. 5(c) portrays a markedly smoother surface when the inhibitor is present at a conc. of $10^{-2}$ M. This observation specifies the creation of a protective layer facilitated by the absorption of the inhibitor onto the metal surface. These SEM images provide visual confirmation of the inhibitive effects of [EMIM]Cl on mild steel corrosion, corroborating the findings obtained through quantitative analyses [20-22].

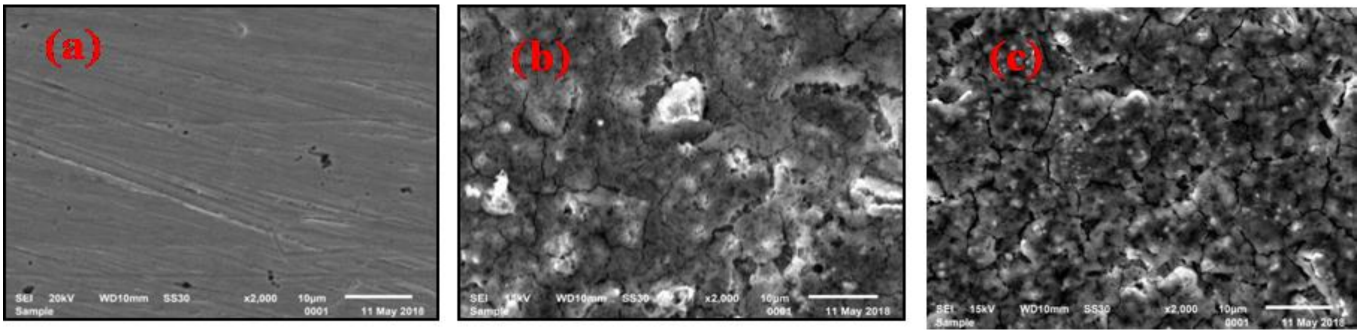

**Fig. 5** SEM micrographs of mild steel: (a) polished mild steel, (b) mild steel in 0.5 M $H_2SO_4$ and (c) mild steel in 0.5 M $H_2SO_4$ with the presence of inhibitor.

### 3.4.2 AFM (Atomic force microscopy)

Fig. 6 shows the 3-dimensional atomic force microscopy (AFM) micrographs of mild steel (MS), providing insights into the surface topography at a nanoscale level. In addition to visual representation, quantitative characteristics of the metal surface, including area and line roughness, were meticulously examined using AFM analysis. For plain MS and MS immersed in acid, the line and area roughness were determined to be 26.22 nm & 67.41 nm, and 760.48 nm & 461.26 nm, respectively. Remarkably, with the addition of ($10^{-2}$ M) concentration of inhibitor, the roughness of the line and area was decreased significantly to 386.29 nm and 206.16 nm, respectively, compared to the acid-treated MS. The decreased surface roughness can be attributed to the absorption of inhibitor molecules onto the surface of MS. This process facilitates the formation of a protective layer resulting in surface smoothness. These quantitative findings further support the inhibitory effects of [EMIM]Cl on mild steel corrosion and emphasize the potential for surface modification through inhibitor application [23].

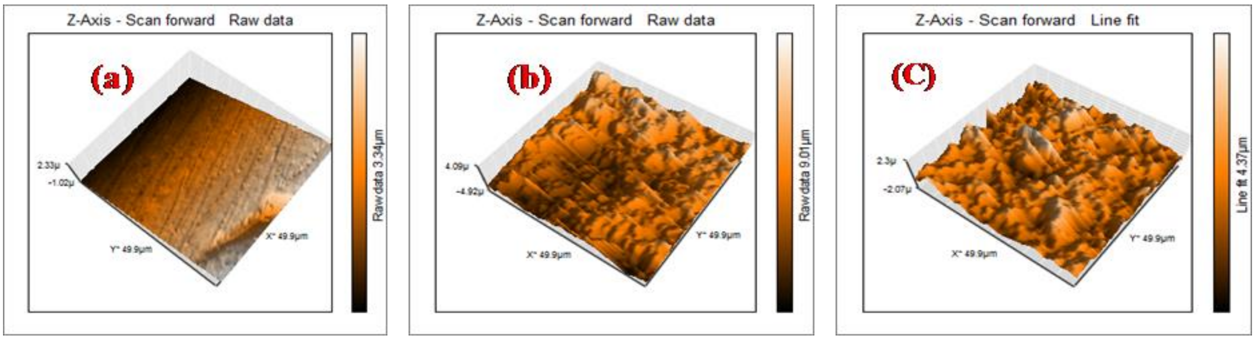

**Fig.6** AFM micrographs of (a) polished mild steel (b) mild steel in 0.5M $H_2SO_4$ (c) mild steel in 0.5M $H_2SO_4$ in the presence of inhibitor.

## 4. Conclusions

Electrochemical impedance spectroscopy, weight loss, and potentiodynamic polarization studies have identified [EMIM]Cl (1-ethyl-3-methyl imidazolium chloride) to be highly efficient in the process of corrosion inhibition of a substance such as mild steel in an $H_2SO_4$ solution of 0.5M concentration. The [EMIM]Cl at 298K and $10^{-2}$ M concentration was found to be a highly effective corrosion inhibitor to mild steel with a corrosion inhibition efficiency of 94. 51%. Hence this has pointed out that the protective ability of [EMIM]Cl is significant under these circumstances. Further, the experiments conducted also showed that the increase in the concentration of [EMIM]Cl was directly proportional to inhibition efficiency which gives an implication that the compound is efficient as an inhibitor even when used in small quantities. The findings of electrochemical impedance spectroscopy studies using the Nyquist plot were found to confirm that the existence of the ionic liquid inhibitor on the mild steel surface leads to a reduction in the capacity of the double layer and an increase in the charge transfer resistance, the generally desirable trends in the corrosion inhibition process. On the other hand, through the potentiodynamic polarization tests, it was evidenced that the [EMIM]Cl possesses a dual inhibition. Last, the surface morphology studies were determined by using electron microscopy and atomic force microscopy wherein the result observed the formation of a thin layer of a substance on the surface of mild steel due to [EMIM]Cl, which testified to the inhibiting action of the said ionic liquid. Altogether, the nature of the obtained results is explicit and unambiguous to evidence 1-ethyl-3-methylimidazolium chloride as a green corrosion inhibitor of mild steel under the influence of sulfuric acid.

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## Conflict of interest

There is no conflict of interest

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