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Experimental and Surface Morphological Studies of Imidazolium-based Ionic Liquid as Corrosion Inhibitor for Mild Steel in Sulphuric Acid Medium

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The corrosion inhibitor 1-butyl-3-methylimidazolium chloride [(BMIM)Cl], an ionic liquid, was used to determine the potency of inhibitor in 0.5 M of H_2SO_4 on the surface of mild steel. The studies performed weight loss measurements over time and electrochemical impedance spectroscopy (EIS). Weight loss studies evaluate the degree of degradation in a mild steel (MS) specimen subjected to sulphuric acid by assessing the reduction in weight of the exposed sample over the duration of exposure. EIS measures the electrochemical properties of the mild steel sample in a sulphuric acid solution interface. Through experimental analysis involving the use of mild steel and ionic liquid, it was established that the material possesses a high potential to reduce the corrosion rate of mild steel in an acidic solution. Also, the surface characterization of the steel sample treated with or without the [(BMIM)Cl] inhibitor in sulphuric acid was characterized using both SEM & AFM techniques. A cross-sectional analysis by SEM and AFM give a physical confirmation of the findings that the ionic liquid, [(BMIM)Cl], when mixed with sulphuric acid, deposits a barrier on the steel surface. The results support the application of [(BMIM)Cl] in preventing corrosion of steel samples in an acidic environment, owing to the formation of a passivating layer through the reaction of the ionic liquid with the metal surface.

Keywords: Corrosion inhibitor, Sulphuric acid, Ionic liquid, Mild steel, Weight loss, Electrochemical studies.

INTRODUCTION

Mild steel, mainly consist of carbon and manganese along with iron, is the most commonly utilized carbon steel in industrial settings where it interacts with acids, bases and salt solutions. The processes of plastic deformation and heat treatment play a vital role in the processing of mild steel and can influence its susceptibility to corrosion. Good machinability and weldability and at the same time competitive price make the mild steel preferable for use in buildings, automobiles, structures and ships, where a high strength price ratio is desirable. Nevertheless, in industrial applications such as acid pickling and descaling, the utilization of sulphuric acid results in severe corrosion and therefore, many monetary losses [1-4]. Corrosion is the process by which metals disintegrate due to their chemical reaction with the surrounding environment, not only altering the aesthetics of the material but also decreasing its durability and, in turn, impacting people's lives and technological advancements. This problem is more acute with generally used metals including iron, aluminium, copper, nickel, zinc, *etc*.

Inhibitors are also among the most effective and cheap means of preventing corrosion. These substances are widely used as they are cheap, easily available, non-hazardous to health, biodegradable and easy to apply [5]. The economic impacts, the effectiveness of the chosen inhibitor and its environmental compatibility are the primary factors influencing the specific suitability of the inhibitor. Some of these molecules attach themselves more easily to the metal surface because of the nature of the molecules or compounds they are made from. More particularly, compounds with heteroatoms with high electronegativity like oxygen, sulphur and nitrogen exhibit areas of high electron density. Also, the multiple bonds like double or triple bonds are also responsible for the localized electron density areas. When these high electron density regions come in contact with a metal surface they covalently adhere. This adsorption occurs because the partial positive charge field by the metal charges the high electron density parts of the organic compound [6,7].

Previous studies have confirmed the performance of imidazolium based ionic liquids as inhibitors in mild steel provide the enhanced mechanical characteristics which make the versatile material suitable for use in the construction, machinery and all kinds of products right from the basic consumer goods to advanced technological applications [8,9]. In more detail, new types of salts containing imidazolium ions have shown a possibility to prevent corrosion of carbon steel C35 and C38 grades, which are used in construction, when they interact with solutions containing acids. While the effectiveness of these imidazole derivatives in the inhibition of corrosion was already known, however, new possibilities for tuning imidazolium salts for the prevention of acid corrosion on particular carbon steel kinds can exhibit better results in terms of corrosion inhibition.

Imidazolium-based ionic liquid [(BMIM)Cl] consists of π-electrons and nitrogen atoms that facilitate their interaction with metal surfaces than other heterocyclic compounds. These compounds are low-cost, can easily be prepared and possess good anti-corrosive tendencies on mild steel [10,11]. This work therefore seeks to determine the inhibition efficiency of [(BMIM)Cl] on mild steel in an acidic solution using weight loss and electro-chemical methods supported by surface characterization using SEM and AFM techniques.

EXPERIMENTAL

The specimen mild steel strip consists of 0.15% carbon, 0.08% silicon, 0.02% sulfur, 1.02% manganese, with highest iron constituting at 98.72%. For the weight loss experiments, cubes filled with a solution were fabricated, each with a side length of 1 cm, resulting in a surface area of 1 cm^2 exposed. For the electrochemical tests, the coupons in rectangular shape were prepared with a size of 1 cm × 1 cm × 5 cm.

For the initial preparation of the coupons before starting the experiments, coupon surfaces were first roughened with 100 emery paper and followed by 220, 400, 600, 1000 and 2000 emery papers in order to achieve a smooth surface for further testing of the structure of the specimen. To avoid any residual on the samples, the last step was to rinse them with double distilled water after polishing. A freshly 0.5 M sulphuric acid solution was prepared after dilution from conc. sulphuric acid.

Weight loss measurements: The weights of the samples were recorded before and after immersion to calculate the weight loss using using a Mettler Toledo analytical balance. The mild steel coupons as specimens were exposed to 0.5 M sulphuric acid solution. In brief, a series of solution of 100 mL acid solutions with varying corrosion inhibitor concentrations were prepared followed by the complete immersion of the mild steel coupons and then left for 6 h. After that, the steel coupons were removed, rinsed and blotted to eliminate any disengaged corrosion products and then weighed to assess the weight loss due to corrosion. The specimens maintained in solutions with higher concentrations of inhibitor compounds were expected to exhibit reduced weight loss in comparison to the control sample without inhibitor, provided that the inhibitor effectively mitigates the acid corrosion of the metal surface. The variations in weight loss observed after 6 h of acid exposure and the different concentrations of the inhibitor compound, the effectiveness of the inhibitor, along with its optimal dosage, was determined with 10^{-2} M, 10^{-3} M, 10^{-4} M and 10^{-5} M at 25 ºC.

Electrochemical studies: The electrochemical experiments were performed using a conventional three-electrode cell assembly setup to evaluate the corrosion protection on the mild steel coupons. The platinum electrode was used as the counter electrode while the saturated calomel electrode (SCE) was used as the reference electrode. The experiments were conducted at 25 ºC using 0.5 M H_2SO_4 electrolyte solution. The effect of varying concentrations of inhibitor compound (10^{-2} M, 10^{-3} M, 10^{-4} M and 10^{-5} M) were examined. The EIS measurements were conducted with a 5 mV AC amplitude across a frequency range of 100 kHz to 0.01 Hz for the open circuit potential, with a scan rate of 1 mV/s.

Surface characterization (SEM and AFM) analysis: A Jeol JSM-6610LV at high-resolution scanning electron microscope was used to obtain high quality SEM micrographs. The 3D surface profiles of the inhibitors were obtained by atomic force microscopy (AFM) with an AG Nano surf atomic force microscope consisted a 10 nm radius tip and a 0.1 N/m spring constant for a better identification of inhibitory efficiency.

RESULTS AND DISCUSSION

Measurements of weight loss: At 25 ºC, the weight lost due to corrosion at the varying concentrations of 10^{-2} M, 10^{-3} M, 10^{-4} M and 10^{-5} M inhibitors in 0.5 M H_2SO_4 medium. The inhibition efficiency (η_{WLM}, %) was determined using eqn. 1 [12-14]:

$$\eta_{WLM}\ (\%) = \left(\frac{\text{C.R. acid} - \text{C.R. inhibitor}}{\text{C.R. acid}}\right) \times 100 \quad (1)$$

where CR represents the rate of corrosion and calculated by the following eqn. 2:

$$\text{C.R. (acid or inhibitor)} = \frac{W_{initial} - W_{final}}{S \times t} \quad (2)$$

here, $W_{initial}$ is the polished initial weight of mild steel (g); W_{final} is the mild steel weight later 6 h immersion (g); S is the mild steel surface area (cm^2) and t is the immersion time (h).

Table-1 shows that there is a direct correlation between the concentration of the inhibitor and its inhibition efficiency; as the concentration of the inhibitor increases, the corrosion rate decreases and the inhibition efficiency rises, from 72.76% to 85.86%.

Electrochemical impedance spectroscopy (EIS) studies: The mild steel samples were subjected to 0.5 M H_2SO_4 solutions, both with and without varying amounts (10^{-2} M, 10^{-3} M, 10^{-4} M and 10^{-5} M) of inhibitor for 1 h to obtain stabilized OPC. The Nyquist plots (Fig. 1) illustrate the impedance behaviour for mild steel in the presence and absence of sulphuric acid solution containing ionic liquid as inhibitor at different

TABLE-1
CORROSION PARAMETERS OF MILD STEEL 0.5 M SULPHURIC ACID WITH OTHER CONCENTRATIONS OF [(BMIM)Cl] AT 25 °C

Conc. inhibitor (Molarity)	Corrosion rate (g/cm^2/h)	Inhibition efficiency (%)	Surface coverage (θ)
Blank	0.7002	–	–
10^{-5}	0.1766	72.76	0.7276
10^{-4}	0.1361	79.85	0.7985
10^{-3}	0.1188	82.83	0.8283
10^{-2}	0.0948	85.86	0.8586

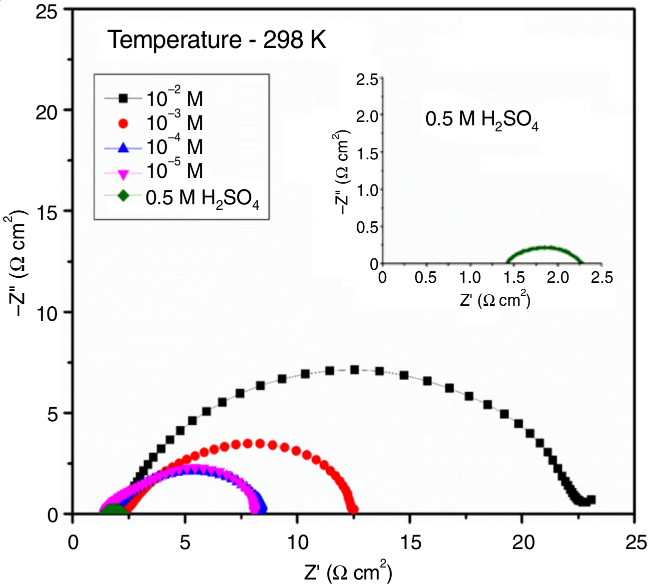

Fig. 1. Nyquist plot in 0.5 M sulphuric acid for mild steel with and without concentration of [(BMIM)Cl] at 25 °C

concentrations. Larger diameter semicircles indicate improved corrosion resistance attributed to increased surface impedance from inhibitor adsorption. The R_{ct} values calculated based on the diameter of the Nyquist semicircles presented an increase in the [(BMIM)Cl] concentration, which indicates that the presence of ionic liquid on the mild steel surface slows down the charge transfer processes. The inhibition efficiency (IE%) measures this corrosion protection capability of ionic liquid. The summarized data of R_{ct} and IE% in Table-2 demonstrate the continuous increase in these parameters with the inhibitor concentration which is due to a higher extent of coverage of the metal interface by the ionic liquid. These findings confirmed that [(BMIM)Cl] possessed corrosion inhibition properties for steel in sulphuric acid solutions by adsorbed film formation.

TABLE-2
EIS PARAMETERS FOR MILD STEEL 0.5 M SULPHURIC ACID WITH DIFFERENT CONCENTRATIONS OF [(BMIM)Cl] AT 25 °C

Inhibitor dose (Molarity)	R_{ct} (Ω cm^2)	f_{ma} (Hz)	C_{dl} (µF cm^{-2})	Inhibition efficiency (%)
Blank	1.090	0.219	667111.40	–
10^{-5}	7.080	2.344	9596.00	84.94
10^{-4}	7.869	2.204	9181.89	86.14
10^{-3}	10.900	3.564	4099.03	90.00
10^{-2}	22.194	7.217	994.14	95.07

The efficiency of inhibition was calculated using eqn. 3 [15-17]:

$$\text{IE (\%)} = \frac{R_{ct} - R^{o}_{ct}}{R_{ct}} \times 100$$

where R_{ct} and R^{o}_{ct} represent the charge transfer resistance in the presence and absence of the inhibitor, presenting an estimation of the inhibitor's effect on corrosion rates.

The double-layer capacitance (C_{dl}) was determined using the following relation:

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

where R_{ct} is the charge transfer resistance; and f_{max} is the frequency at the maximum impedance at an imaginary component.

The results indicated that R_{ct} values increased upon adding [(BMIM)Cl], with the efficiency of the highest inhibition is 95.07% observed at a concentration of 10^{-2} M. Furthermore, the double layer capacitance (C_{dl}) decreased, as the increased thickness of the double-layer, related to the adsorption of inhibitor molecules on the metal surface, accounts for the lowered corrosion rate by restricting the movement of reacting species involved in the dissolution of metal [18-21].

Surface characterization

SEM studies: The SEM micrographs of the mild steel surface exposed to the ionic liquid [(BMIM)Cl)] are shown in Fig. 2, demonstrating that the ionic liquid effectively protected mild steel from corrosion when subjected to a 0.5 M H_2SO_4 solution with 10^{-2} M inhibitor for 6 h at 25 ºC. Without the inhibitor, the surface of mild steel developed various defects including cavities, pits, cracks as well as huge deposits of corrosion products as shown in Fig. 2a. On the other hand, the mild steel sample immersed in the inhibitor-containing an acidic solution revealed that the surface morphological study under SEM was comparatively smoother and hence testified that the corrosion was controlled to a large extent. This proves that the [(BMIM)Cl]$^-$ ions adhered to the metallic surface and prevented the attack by forming an inhibiting barrier film. The high concentration yielded better adsorption of the inhibitors on the surface in addition to better coverage hence enhancing the corrosion protection. Consequently, upon reviewing the SEM images, there is strong visual evidence that [(BMIM)Cl] serves as an effective ecofriendly corrosion inhibitor for mild steel in sulphuric acid medium, particularly at lower temperatures due to its adsorption on the substrate surface. This minimizes the interaction between the corrosive acid and the steel surface, thereby decreasing the corrosion rate [22-25].

Atomic force microscopy (AFM) studies: Fig. 3 shows the atomic force microscopic images of mild steel samples before and after the acidic solution exposure. The mild steel sample exhibited a rough surface following contact with the acid since it corroded faster than the mild steel with an inhibitor protection. The corrosion inhibitor reduces the contact of the sulphuric acid solution on the mild steel surface due and the surface becomes to be much smoother. The recorded surface roughness values were found to be 166.69 nm for the inhibitor

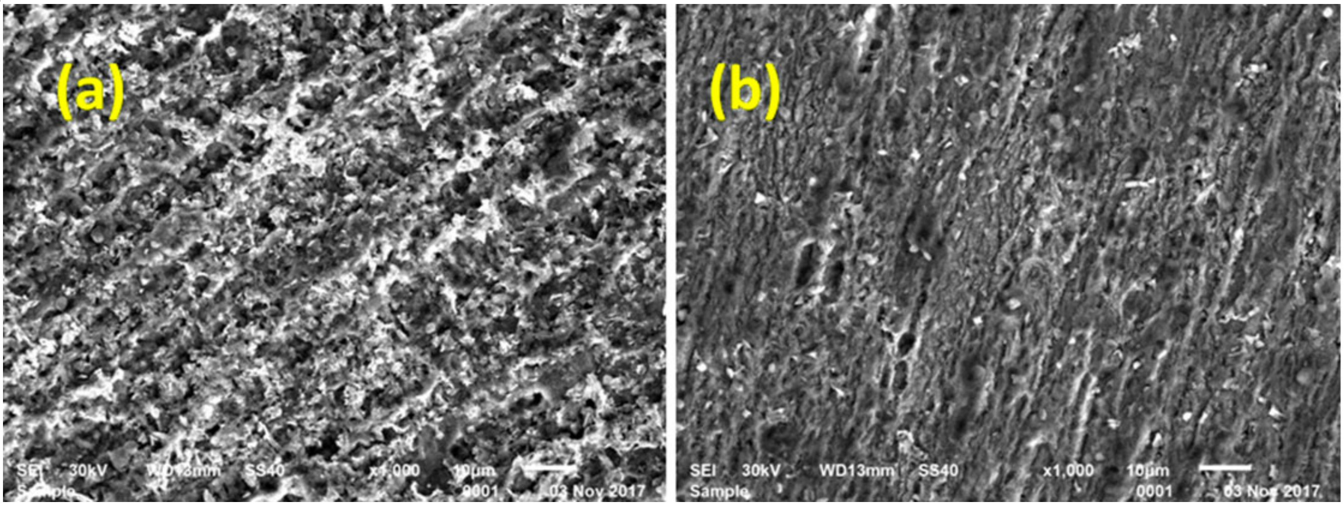

Fig. 2. SEM images of (a) MS in 0.5 M H_2SO_4, (b) MS in 0.5 M H_2SO_4 with [(BMIM)Cl]

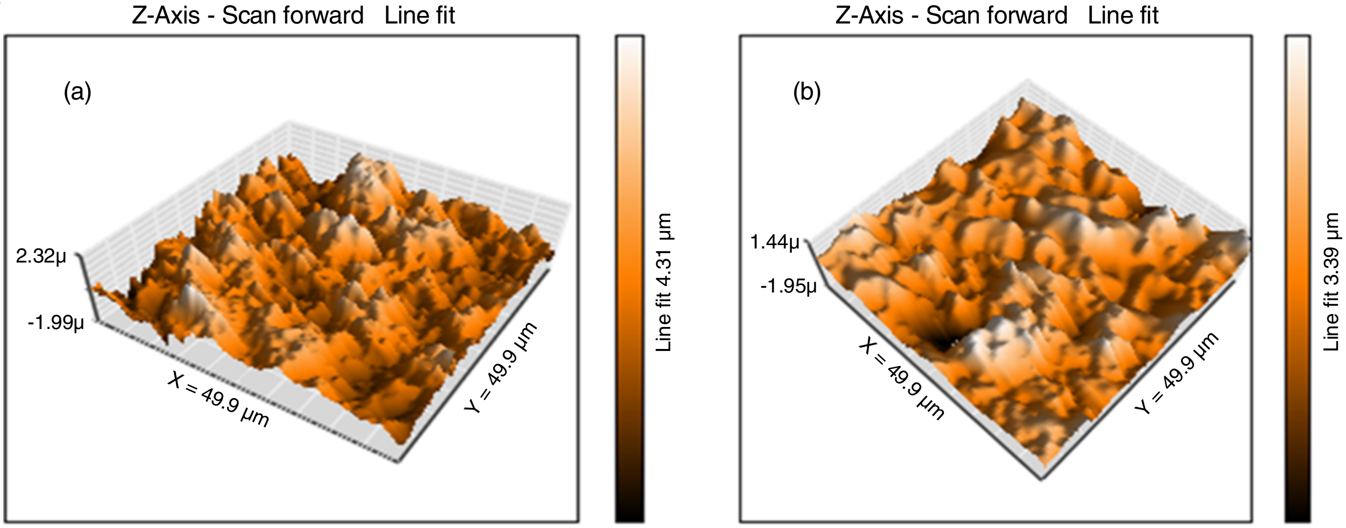

Fig. 3. AFM micrographs of (a) mild steel in 0.5 M H_2SO_4, (b) mild steel 0.5 M H_2SO_4 with [(BMIM)Cl]

treated sample and 254.28 nm for the untreated sample. The decrease in roughness indicates that the [(BMIM)Cl] molecules have successfully adsorbed onto the mild steel surface, hence providing the corrosion protection [26-29].

Conclusion

In this study, the effectiveness of ionic liquid *viz.* 1-butyl-3-methylimadazolium chloride [(BMIM)Cl)] as an inhibitor to corrosion of mild steel in 0.5 M sulphuric acid was successfully analyzed. From the weight loss measurements and electrochemical impedance spectroscopy (EIS) demonstrated that the ionic liquid effectively reduced the corrosion of mild steel. The observed results indicated that the inhibition efficiency of the ionic liquid increased with its concentration, suggesting that the inhibitor molecules interact with the mild steel surface. Moreover, EIS revealed that the charge transfer resistance (R_{ct}) increased and double layer capacitance (C_{dl}) has reduced with increased concentration of ionic liquid. The SEM and AFM analyses of the chemical composition and microstructure confirmed the formation of a strong layer on the surface, effectively shielding it from environmental corrosion.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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