International Research Journal of Natural and Applied Sciences
I F 3.827 Volume 3, Issue 3, March 2016 ISSN: (2349-4077)

Website- www.aarf.asia, Email : editor@aarf.asia , editoraarf@gmail.com

Anti-corrosive properties of 1-Ethyl-3-methylimidazolium tetrafluoroborate on mild steel corrosion in Sulphuric acid Solution.

Anita Kumari*[a,c], Gurmeet Kaur[b,c], Raj Kishore Sharma[c], Gurmeet Singh[c*]
[a]Department of Chemistry, Miranda House, Delhi-110007,
[b]Department of Chemistry, SGTB Khalsa College, Delhi-110007.
[c]Department of Chemistry, University of Delhi, Delhi -110007
[c*]Department of Chemistry, University of Delhi, Delhi -110007

Abstract: Anti-corrosion activity and adsorption nature of 1-Ethyl-3-methylimidazolium tetrafluoroborate [(EMIM) BF_4] has been inverstigated for mild steel in 0.5 M H_2SO_4 medium using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization method.These studies were carried out at various concentrations of this inhibitor. Results obtained for the investigated compound exhibited good corrosion inhibition performance for MS in 0.5M H_2SO_4. The highest inhibition efficiency obtained was 91.60 % [(EMIM) BF_4] at 10^{-2} M. Surface characterization techniques i.e. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the surface morphology of metal surface in the absence and presence of inhibitor.The maximum inhibition efficiency was achieved at 10^{-2} M inhibitor concentration.Tafel polarization studies revealed that [(EMIM) BF_4] acts as mixed-type of inhibitor and form a protective layer on the surface of mild steel. The adsorption of the inhibitor on mild steel surface obeys the Langmuir adsorption isotherm.
Keywords: Mild steel, weight loss, electrochemical studies, SEM, AFM.

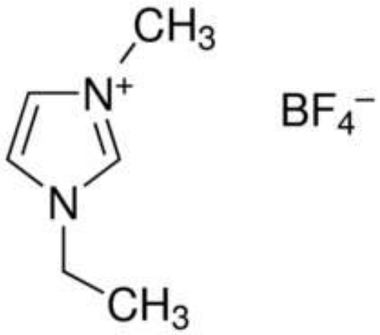
1. Introduction

Mild steel is extensively used as a construction material in heat exchangers, petroleum and refining industries etc. due to its low cost and high mechanical properties. Acidic solutions are used in these industries for acid pickling, acid cleaning, acid descaling and oil wet cleaning that causes corrosion in metals [1-2]. Sulphuric acid (H_2SO_4) and Hydrochloric acid (HCl) are generally used for various applications which are very corrosive in nature and hence it attacks on the mild steel surface and initiate scorrosion. Acid solutions are used to remove undesirable scale formation on metals. This corrosion can cause serious damage to the metal and degrade its properties [3-4]. Corrosion inhibitors play very important role to protect metals from corrosion. These inhibitors usually adsorb on the metal surface forming protective film by chemisorption or physical adsorption and block the active sites on the metal surface. Chemical inhibitors are used to decrease the rate of corrosion processes. The corrosion on metals in acid solutions can be inhibited by organic compounds which mostly contain delocalised electrons or those containing hetero atoms like nitrogen, phosphorus, oxygen and sulphur [5-9].

As earlier reported some ionic liquids compounds are effective corrosion inhibitors in an acidic solution for mild steel. Although several effective inhibitors have been introduced by various researchers previously [10-15] but Imidazole and its derivatives are considered nontoxic compounds and have been studied as corrosion inhibitors [16].

In the present work, ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate [(EMIM) BF_4] has been selected as corrosion inhibitor because it contains heteroatoms which can easily be adsorbed on the mild steel surface and prevent the metal from corrosion in acidic solution.The investigated [(EMIM) BF_4] molecule has been used to evaluate the inhibition efficiency on corrosion of mild steel in 0.5 M H_2SO_4 at various concentrations by using gravimetric measurement, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. In addition, surface morphology of mild steel (MS) is investigated by using SEM and AFM techniques. The [(EMIM) BF_4] molecule has the required properties to show anti corrosion activities. The chemical name and molecular structure of the [(EMIM) BF_4] are listed in Table 1.

Table 1: Name and structure of [(EMIM) BF_4]

1-Ethyl-3-methylimidazolium tetrafluoroborate [(EMIM) BF_4]		
Molecular Formula	$C_6 H_{11}BF_4 N_2$	
Molecular Weight	197.97 g/mol	
Assay	97 %	
Boiling Point	~ 350 ^oC	
Physical State	Liquid	
Solubility in Water	Soluble	

2. Experimental

2.1 Material and test solution

The mild steel coupons having composition (in %): C-0.15, Si-0.08, S-0.02, Mn-1.02 and balance Fe were used for this study. Mild steel coupons having dimensions 4 cm × 1 cm × 1 cm with 1 cm^2 exposed area were selected for working electrode in a three-electrode cell assembly for all electrochemical experiments and rest surface of mild steel were covered by epoxy resin whose one end is connected internally with the copper wire. These coupons were used for corrosion test. The 0.5 M H_2SO_4 solution was prepared by diluting concentrated H_2SO_4 (AR) using double distilled water. The samples were polished using emery sheets of different grades (100, 220, 400, 600, 1000 and 2000) and then washed with double distilled water.

2.2 Weight loss measurements:

Weight loss method is technically the best method for testing the corrosion rate of mild steel as compared to other techniques. Mild steel coupons were immersed in 100 mL of 0.5 M H_2SO_4 for 6 hours in the presence and absence of various concentrations of inhibitor (10^{-2} M, 10^{-3} M, 10^{-4} M and 10^{-5} M) at 298K temperature. Weighed the samples before and after 6 h of immersion time and difference in weights were calculated. Weight Loss Measurements were carried out using analytical weighing machine Mettler Toledo.

2.3 Electrochemical measurements:.

Three electrode assembly was used to perform the electrochemical experiments by using an electrochemical analyzer CHI 760c (CH Instruments, Inc., USA). Mild steel coupons as working electrode, a platinum electrode as counter electrode and saturated calomel electrode (SCE) is used as the reference electrode. The experiments were conducted at 298K in 0.5M H_2SO_4 solution. The inhibitor with the concentration range 10^{-2} M to 10^{-5} M was added to the corrosive medium. The electrode potential was measured against the SCE and the polarization curves were recorded at an examining rate of 1 mV/s with various potential from the detected open circuit potential (OCP), following 1 h of immersion. Before doing the experimental work, the coupons of mild steel were grinded with different emery papers (grade 100, 220, 320, 400, 600, 1000 and 1500) rinsed with double distilled water, degreased with acetone and cleaned in an ultrasonic cleaner. The electrochemical impedance measurements performed at an open circuit potential in a frequency range of 100 kHz down to 10 MHz with 5 mV peak-to-peak amplitude using the AC signal and the Tafel curves were carried out at a scan rate of 0.01 mVs^{-1}.

2.4 Surface characterization (SEM, AFM) studies:

The surface morphology of mild steel coupons having surface area (1 cm × 1 cm × 2 mm) immersed in 0.5M H_2SO_4 solution in the presence and absence of inhibitor for 6 hours was carried out. Samples were taken out from the test solutions without touching the surface. SEM and AFM were used to study the surface morphology of mild steel samples in the absence and presence of inhibitor at highest concentration (10^{-2} M) to observe the extent of inhibition for 6 hours. Mild steel samples were used for surface characterization (SEM and AFM) studies. SEM-images were performed with Jeol Japan, Model No. JSM-6610LV instrument. To enhance the surface morphology, AFM instrument (AG Nanosurf NaioAFM, Switzerland) was used for taking the microscopic 3-dimension images.

3. Results and discussion

3.1 Weight Loss Measurements

Corrosion rate (CR) and corrosion inhibition efficiency (η%) were obtained from weight loss measurements. It is observed from Table 2, that the corrosion inhibition efficiency (η%) increases significantly with increase in the concentration of the investigated inhibitor and decreases with increase in temperature. With the increase in the inhibition efficiency, the adsorption amount of inhibitor molecule increases on the surface of mild steel [17]. Due to the adsorption on the surface of mild steel, it forms protective layers that shield the mild steel from corrosion.

The corrosion rate is calculated by the given equation:

$$C_r\ (\text{acid or inh.}) = \frac{W_{initial} - W_{final}}{S \times t} \quad (1)$$

$W_{initial}$ = weight of the plain polished MS coupons (g)

W_{final} = weight of the MS coupons after 6 hours immersion (g)

S = Surface area of the MS coupon (cm^2)

t = Time (h)

The inhibition efficiency (η %) was calculated by the following equation [18]

$$\eta_{\%} = \frac{C_r^0 - C_r^i}{C_r^0} \text{ X } 100 \quad (2)$$

Where C_r^0 and C_r^i are the corrosion rates of mild steel in the absence and presence of the inhibitor respectively.

The corrosion rate (g cm^{-2} h^{-1}) of mild steel decreases as the concentration of inhibitor increases. It can be seen from the results that on increasing the concentrations of inhibitor, inhibition efficiency increases from 81.91 % to 91.60 % is shown in Fig.1**.**

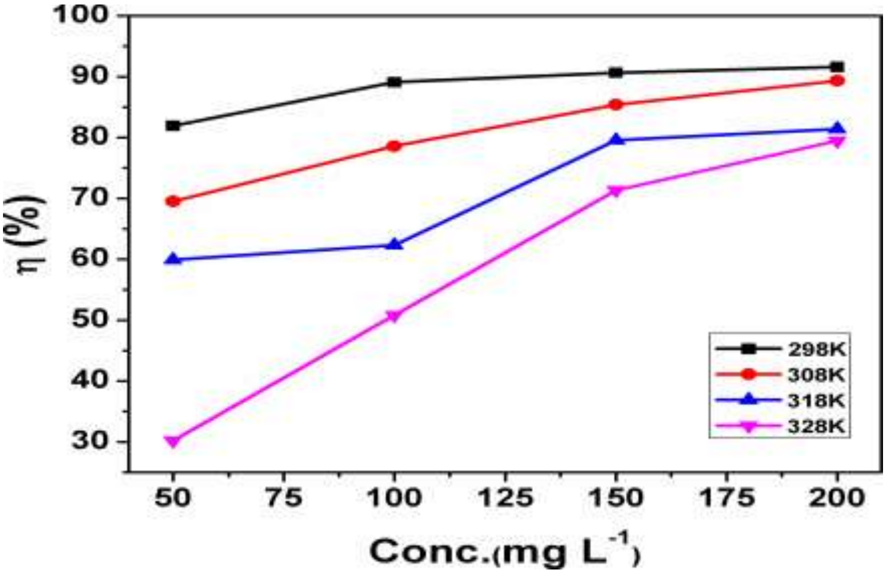


Fig.1. Effect of inhibitor concentrations on corrosion rate and inhibition efficiency at 298K for MS in 0.5M H_2SO_4.

Table 2: Corrosion parameters for mild steel in 0.5 M H_2SO_4 in the absence and presence of various concentrations of 1-Ethyl-3-methylimidazolium tetrafluoroborate [(EMIM) BF_4] at 298 K.

Temp. (K)	**Conc. (mg L^{-1})**	**W_{loss} (g)**	**C.R. (g cm^{-2} h^{-1})**	**η_{WLM} (%)**
298	10^{-5}	0.0211	0.1266	81.91
	10^{-4}	0.0127	0.0762	89.11
	10^{-3}	0.0109	0.0654	90.65
	10^{-2}	0.0098	0.0588	91.60
0.5M H_2SO_4	Blank	0.1167	0.7002	--

3.2 Electrochemical impedance spectroscopy (EIS)

For studying the impedance parameters of mild steel specimen in 0.5 M H_2SO_4 with various concentrations of inhibitor at 298 K the working electrode was immersed into test solution for 1 h at 298 K to attain the steady state potential. The results are shown in Table 3**.** Nyquist plots for mild steel with and without inhibitor are shown in Fig.2**.** The results are shown in Table 3. Increasing [(EMIM) BF_4] concentration enlarges the diameter of the capacitive loop from 10^{-5} M to 10^{-2} M which implies increase in inhibition for mild steel.

Table 3: EIS parameters for mild steel in 0.5M H_2SO_4 in the absence and presence of different concentrations of [(EMIM) BF_4] at 298 K.

Concentration of inhibitor (M)	R_{ct} (Ω cm^2)	f_{max} (Hz)	R_s (Ω cm^2)	Efficiency (IE %)
00	5.47	2.29	1.58	-
10^{-5}	5.80	1.79	1.25	5.69
10^{-4}	8.82	3.14	1.64	37.98
10^{-3}	48.89	21.25	1.84	88.81
10^{-2}	61.19	20.54	1.86	91.06

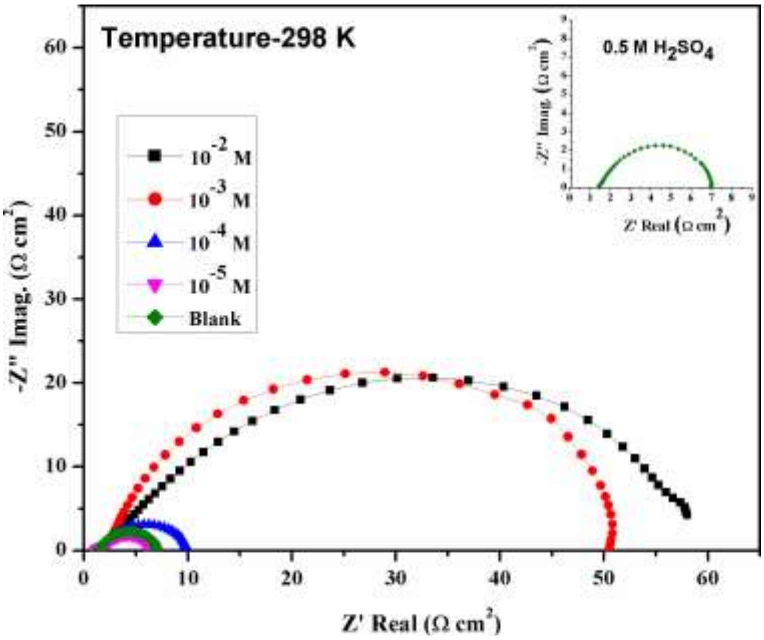


Fig. 2. Nyquist Plots of mild steel in 0.5M H_2SO_4 at 298 K in the presence and absence of various concentrations of inhibitor.

The inhibition efficiency based on impedance study can be calculated by using the following formula [19].

$$IE(\%) = \frac{R_{ct} - R_{ct}^{0}}{R_{ct}} \times 100 \tag{3}$$

Where R_{ct} and R_{ct}^{0} are the charge transfer resistance with and without the inhibitor, respectively.

The result shows that the values of Rct increases on the addition of [(EMIM) BF_4] and inhibition efficiency was 91.06 % at 10^{-2} M concentration of inhibitor. The double layer capacitance (Cdl) decreases due to the increase in double layer thickness via adsorption of the inhibitor molecules on MS surface.

The double layer capacitance, C_{dl} is also calculated using the following relation

$$C_{dl} = \frac{1}{2\pi f_{max} . R_{ct}} \tag{4}$$

Where R_{ct} is the charge transfer resistance and f_{max} is the maximum frequency in Nyquist plot.

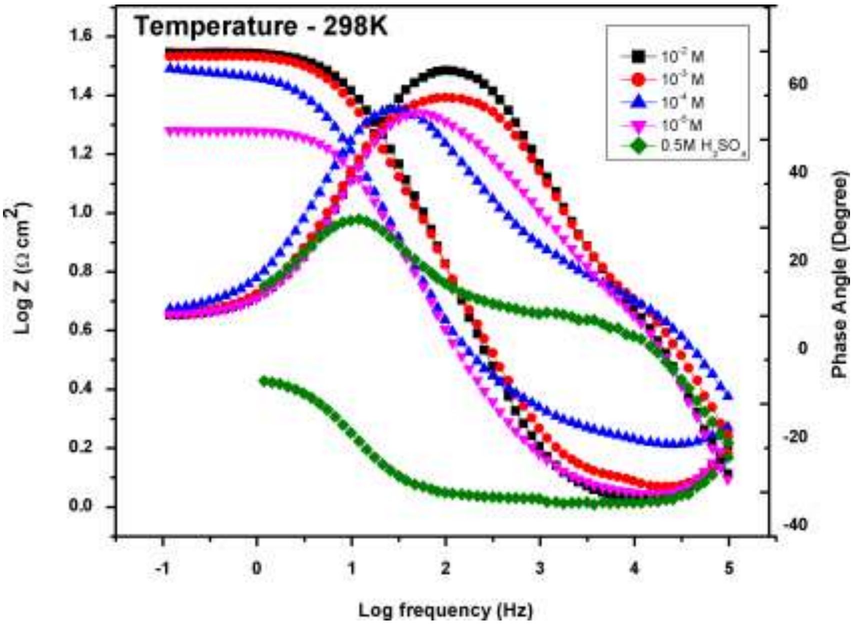


Fig.3. Bode (Log Z Vs. Log Freq.) and Phase angle plot of mild steel in 0.5M H_2SO_4 at 298 K in the presence and absence of various concentrations of inhibitor.

The Bode and phase angle plots for mild steel in the presence and absence of various concentrations of investigated inhibitor are shown in Fig 3. It is observed that the value of impedence increases with the increasing concentrations of inhibitor. An ideal capacitor behavior would result if a slope value attains −1 and phase angle values attain −90° [20]. The investigated inhibitor formed the protective layer on the surface of mild steel in acidic medium which prevents the MS from corrosion.

3.3 Potentiodynamic polarization measurements

The potentiodynamic polarisation curves were recorded for different inhibitor concentrations, which are represented in Fig.4. The parameters obtained from polarisation curves such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (βc and βa) and inhibition efficiency are listed inTable 4, it can be seen from the observations that I_{corr} value is decreased with increase in the concentration of inhibitor.

The following relation is used to evaluate the inhibition efficiencies [21]

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

Where i_{0corr} and i_{icorr} are the values of the corrosion current density for MS in 0.5M H_2SO_4 solution in absence and presence of inhibitor respectively.

Table 4: Polarization parameters for mild steel in 0.5M H_2SO_4 without and with different concentrations of [(EMIM) BF_4] at 298 K.

Inhibitor concentration (M)	$-E_{corr}$ (mV vs. SCE)	i_{corr} (μA cm^{-2})	$β_a$ (mV/dec)	$-β_c$ (mV/dec)	Inhibition efficiency (IE%)
00	516	4734.00	157.90	158.00	-
10^{-5}	507	4024.00	128.20	125.72	14.99
10^{-4}	491	1571.00	112.66	135.17	66.81
10^{-3}	509	1271.00	149.56	152.50	73.15
10^{-2}	500	624.30	81.36	132.41	86.81

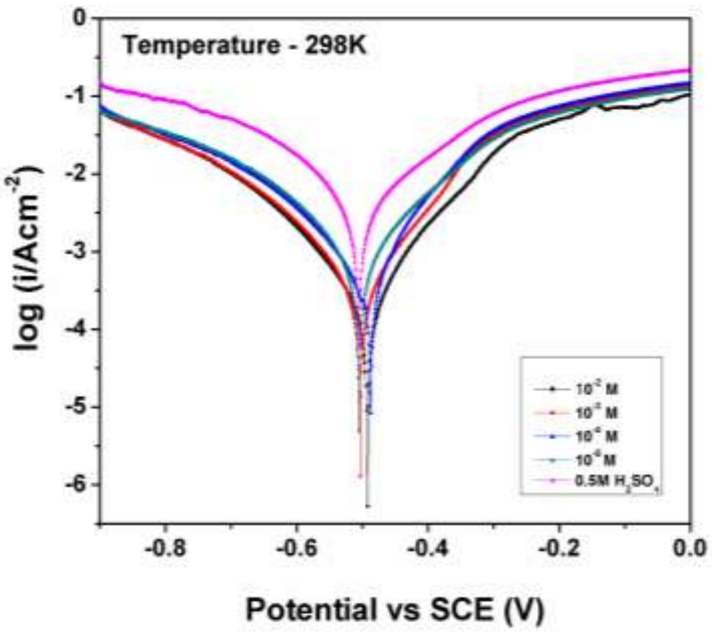


Fig.4. Polarisation curves for MS in 0.5M H_2SO_4 in the absence and presence of different concentrations of inhibitor at 298K.

The polarization curve is represented in Fig 4 indicating both anodic and cathodic currents in the presence of inhibitor as compared to without inhibitor. The results show that the inhibition efficiency increases with decreasing values of i_{corr} but decreases with increasing temperature due to desorption of the absorbed inhibitor molecule from the mild steel surface [22].

As reported in the earlier literature that if the value of $E_{corr} > 85$ mV with respect to E_{corr} values of blank solution, the inhibitor behave as a cathodic or anodic inhibitor, and if $E_{corr} <$ 85 mV, the inhibitor acts as mixed type inhibitor [23-24]. It is obtained from Table 4 that the shift in E_{corr} value is less than 85mV therefore the investigated inhibitor [(EMIM) BF_4] acts as a mixed type of inhibitor.

3.4 Surface characterization

SEM images were taken to investigate the surface Morphology of polished mild steel in the presence and absence of investigated inhibitor. Mild steel immersed in 0.5 M sulphuric acid solution and in the presence of highest concentration of inhibitor (10^{-2} M) for 6 h at 298 K shows less corrosion. Fig 5 shows the high damaged and rough surface due to attack by acid solution while in presence of inhibitor shows less damaged surface. This is revealed that higher concentration of inhibitor formed protective layer by adsorption on the surface of mild steel [25].

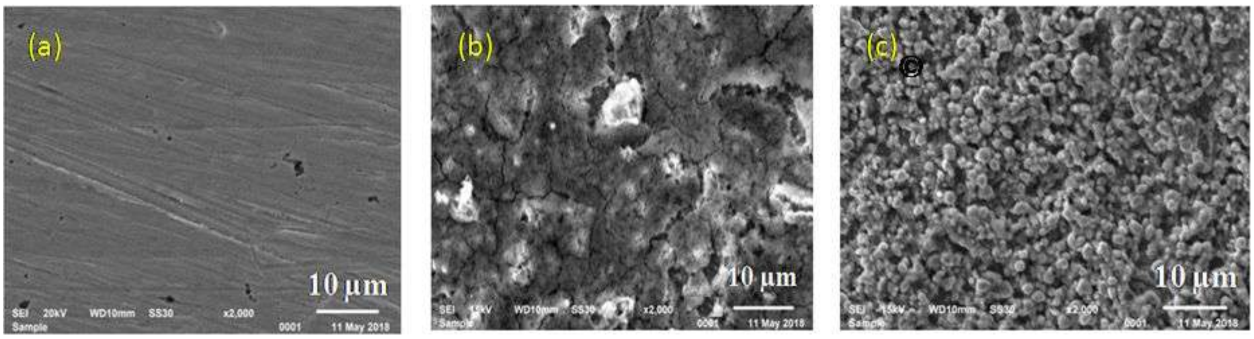


Fig.5. SEM images of (a) polished mild steel (b) mild steel in 0.5 M H_2SO_4, (c) mild steel in 0.5M H_2SO_4 with inhibitor.

AFM was used to investigate the quantitative parameters such as line roughness and area roughness of metal surface. Fig.6 represents the 3D AFM images of mild steel before and after immersion for 6 hours in 0.5M H_2SO_4 in the presence and absence of the inhibitor. The line and area roughness for acid immersed MS is 760.48 nm and 461.26 nm respectively and in the presence of highest concentration of inhibitor (10^{-2} M) the line and area roughness decreased i.e. 240.61 nm and 362.20 nm respectively as compared to acid treated mild steel alone. SEM and AFM images of mild steel indicated that reduction of corrosion rate by adsorption of [(EMIM) BF_4] on the mild steel surface [26].

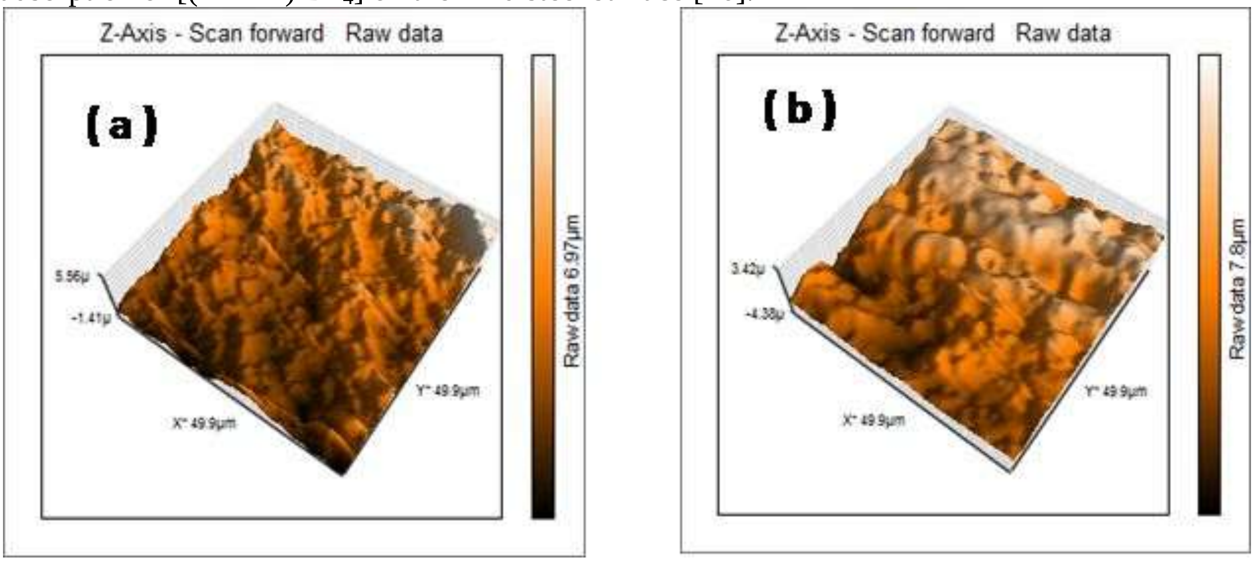


Fig.6. AFM images of (a) mild steel in 0.5M H_2SO_4, (b) mild steel in 0.5M H_2SO_4 with inhibitor.

4. Conclusions

The investigated 1-Ethyl-3-methylimidazolium tetrafluoroborate [(EMIM) BF_4] is efficient corrosion inhibitor for mild steel in 0.5M H_2SO_4. The inhibition efficiency of studied inhibitor obtained from weight loss and electrochemical studies are very well correlated with the data obtained experimentally. The inhibition efficiency of studied inhibitor increases with the increase in the concentration of inhibitor. The potentiometric polarisation measurement shows that [(EMIM) BF_4] acts as mixed type of inhibitor. SEM and AFM images of mild steel show that the inhibitor formed the protective layer on the mild steel surface.

References

[1] E. Gutiérrez, J. A. Rodríguez, J. Cruz-borbolla, J. G. Alvarado-rodríguez, and P. Thangarasu, "Development of a predictive model for corrosion inhibition of carbon steel by imidazole and benzimidazole derivatives," vol. 108, pp. 23–35, 2016.

[2] R. Kumar, R. Chopra, G. Singh ,Electrochemical, morphological and theoretical insights of a new environmentally benign organic inhibitor for mild steel corrosion in acidic media,J. Mol. Liq. 241 (2017) 9–19

[3] V. G. Vasudha, S. P. K, Polyalthia longifolia as a corrosion inhibitor for mild steel in HCl solution, Res. J. Chem. Sci., 3 (2013) 21–26.

[4] N. Patel, A. Rawat, S. Jauhari, G. Mehta, Inhibitive action on Bridelia restusa leaves extract on corrosion of mild steel in acidic media, Eur. J. Chem., 1 (2010) 129–133.

[5] Z. Salarvand, M. Amirnasr, M. Talebian, K. Raeissi, S. Meghdadi, Enhanced corrosion resistance of mild steel in 1M HCl solution by trace amount of 2-phenyl-benzothiazole derivatives: Experimental, quantum chemical calculations and molecular dynamics (MD) simulation studies, Corros. Sci., 114 (2017) 133–145.

[6] M. K. Bagga, R. Gadi, O. S. Yadav, R. Kumar, R. Chopra, G. Singh, Investigation of phytochemical components and corrosion inhibition property of Ficus racemosa stem extract on mild steel in H_2SO_4 medium, J. Environ. Chem. Eng., 4 (2016) 4699–4707.

[7] K. H. Hassan, A. A. Khadom, N. H. Kurshed, Citrus aurantium leaves extracts as a sustainable corrosion inhibitor of mild steel in sulfuric acid, South African J. Chem. Eng., 22 (2016) 1–5.

[8] R. Kumar, O. S. Yadav, G. Singh, Electrochemical and surface characterization of a new eco-friendly corrosion inhibitor for mild steel in acidic media : A cumulative study, J. Mol. Liq., 237 (2017) 413–427.

[9] I. Ahamad, M. A. Quraishi, Mebendazole: New and efficient corrosion inhibitor for mild steel in acid medium, Corros. Sci., 52 (2010) 651–656.

[10] J. Kovaˇ and I. Miloˇ, "The roles of mercapto , benzene and methyl groups in the corrosion inhibition of imidazoles on copper : I . Experimental characterization," vol. 98, pp. 107–118, 2015.

[11] M. Mousavi, M. Mohammadalizadeh, and A. Khosravan, "Theoretical investigation of corrosion inhibition effect of imidazole and its derivatives on mild steel using cluster model," vol. 53, pp. 3086–3091, 2011.

[12] L. Zeng, G. A. Zhang, X. P. Guo, and C. W. Chai, "Inhibition effect of thioureidoimidazoline inhibitor for the flow accelerated corrosion of an elbow," vol. 90, pp. 202–215, 2015

[13] S.Kumar Shukla, M.A. Quraishi, R. Prakash, A self doped conducting polymer‘‘polyanthranilic acid": An efficient corrosion inhibitor for mild steel in acid solution,

[14] A. Kokalj, "Formation and structure of inhibitive molecular film of imidazole on iron surface," vol. 68, pp. 195–203, 2013.

[15] H. Otmacic, E. Stupnisek-lisac, and H. Takenouti, "The influence of pH value on the efficiency of imidazole based corrosion inhibitors of copper," vol. 52, pp. 398–405, 2010.

[16] Milo and A. Kokalj, "How relevant is the adsorption bonding of imidazoles and triazoles

for their corrosion inhibition of copper ?," vol. 124, no. April, pp. 25–34, 2017.

[17] S. Shahabi, P. Norouzi, M. R. Ganjali, Electrochemical and theoretical study of the inhibition effect of two synthesized thiosemicarbazide derivatives on carbon steel corrosion in hydrochloric acid solution, RSC Adv., 5 (2015) 20838–20847.

[18] L. Zeng, G. A. Zhang, X. P. Guo, and C. W. Chai, "Inhibition effect of thioureidoimidazoline inhibitor for the flow accelerated corrosion of an elbow," vol. 90, pp. 202–215, 2015.

[19] F. M. Mahgoub, S. M. Al-Rashdi, Investigate the Corrosion Inhibition of Mild Steel in Sulfuric Acid Solution by Thiosemicarbazide, Open J. P. Che.6 (2016) 54-66.

[20] P.Singh, A.Singh, M.A.Quraishi, Thiopyrimidine derivatives as new and effective corrosion inhibitors for mild steel inhydrochloric acid: Electrochemical and quantumchemical studies, J. Taiwan Inst. Chem. Eng. 60 (2016) 588–601

[21] I.Ahamad, R. Prasad, M. A. Quraishi, Experimental and quantum chemical characterization of the adsorption of some Schiff base compounds of phthaloyl thiocarbohydrazide on the mild steel in acid solutions, Mater. Chem. Phys., 124 (2010) 1155–1165.

[22] A.K. Singh, M.A. Quraishi, The effect of some bis-thiadiazole derivatives on the corrosion of mild steel in hydrochloric acid, Corros. Sci. 52 (2010) 1373–1385.

[23] K.F. Khaled, The inhibition of benzimidazole derivatives on corrosion of iron in 1M HCl solutions, Electrochim. Acta 48 (2003) 2493–2503.

[24] D. Daoud, T. Douadi, H. Hamani, S. Chafaa, M. Al-Noaimi, Corrosion inhibition of mild steel by two new S-heterocyclic compounds in 1 M HCl: Experimental and computational study, Corros. Sci., 94 (2015) 21–37.

[25] M. Mahdavian, S. Ashhari,Corrosion inhibition performance of 2-mercaptobenzimidazole and 2-mercaptobenzoxazole compounds for protection of mild steel in hydrochloric acid solution, Electrochimica Acta 55 (2010) 1720–1724.

[26] P. Singh, V. Srivastava, M.A. Quraishi, Novel quinoline derivatives as green corrosion inhibitors formild steel in acidic medium: Electrochemical, SEM, AFM, and XPS studies, J. Mol. Liq. 216 (2016) 164–173.