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# Computational and Electrochemical Characterization of Synthesized Ionic Liquid as a Green Corrosion Inhibitor in 0.5 M H<sub>2</sub>SO<sub>4</sub> Solution for Mild Steel

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## Abstract

The corrosion inhibition characteristics of 3-Butyl-1-methyl-1*H*-benzo (d)-imidazol-3-ium bromide [BMBIm]Br have been studied as eco-friendly green inhibitor for corrosion control of mild steel in  $0.5 \text{ M H}_2\text{SO}_4$  solution by computational and electrochemical methods. The structure of the obtained [BMBIm]Br was confirmed by using <sup>1</sup> H, <sup>13</sup>C NMR, and IR spectroscopy, which also confirms the absence of any major impurities. The corrosion data extracted from Tafel plots, electrochemical impedance spectroscopy and SEM, AFM, EDX indicate high inhibition effectiveness in H<sub>2</sub>SO<sub>4</sub> solution. SEM and EDX observations confirmed the existence of protective inhibitor film on metal surface. The adsorption of an ionic liquid on the mild steel surface follows Langmuir adsorption isotherm. The effect of the temperature on the corrosion behaviour with addition of the different

concentration of [BMBIm]Br was studied in the temperature range of 298 -328 K. Quantum chemical parameters such as highest occupied molecular orbital energy ( $E_{HOMO}$ ), lowest unoccupied molecular orbital energy ( $E_{LUMO}$ ), energy gap ( $\Delta E$ ) and dipole moment ( $\mu$ ) were also calculated. Quantum chemical calculations also supported experimental data and the adsorption of inhibitor molecules onto the metal surface.

Keywords: - Ionic liquid, [BMBIm]Br, Corrosion Inhibition, SEM, EDX, AFM, Green Inhibitor

## Introduction:-

The annual estimated cost of corrosion in the U.S. is \$451 billion or 2.7% of the nation's gross domestic product (IMPACT Study, NACE International, 2016). This enduring cost is in spite of the development of numerous technologies dedicated to providing corrosion protection. In India the cost of corrosion has been estimated to be to the tune of Rs. 2 lakh crores each year i.e. around 6 % of India's GDP (2013) [1]. These aggressive environments are responsible for several types of corrosion, such as general and localized, stress, galvanic, erosion and crevice corrosions, which cause damage in the processing and transportation equipments.[2] In a strong acid medium, the corrosion inhibitors which are widely used to control the corrosion problem of low carbon steel upon exposure to acidic solutions.[3-13]. Organic compounds which contain nitrogen, sulfur, oxygen, heterocyclic with a polar functional group and a conjugated double bond have been reported to inhibit corrosion [14-18]. The term "room temperature ionic liquids (RTILs)" which was coined in 1990s, refers to molten salts having a melting point below 100°C [19].

Almost unlimited variations of RTILs can be synthesized by combining numerous kinds of cations and anions. Therefore, it is possible to extract desirable properties for a specific application by designing RTILs properly. Mild steel corrosion inhibitors have been widely investigated because of their practical applications. It has long been recognised that nitrogen and oxygen, sulphur containing organic compounds act as inhibitors for mild steel dissolution. Among them the most used are benzimidazole [20-25] presenting the former the highest efficiency. The effectiveness of heterocyclic molecules as corrosion inhibitor is based on their chelating action and the formation of an insoluble physical diffusion barrier on the electrode surface, preventing metal reaction and dissolution. Such a barrier is readily formed by nitrogen-containing heterocyclic molecules due to the strong  $\pi$ -interaction between the aromatic rings.

In the present work, the inhibition effect of mild steel on mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub> is studied by Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) measurements, scanning electron microscope (SEM), Energy dispersive X-rays (EDX) analysis and contact angle measurements was utilized to investigate the corrosion protection performance of [BMBIm]Br on steel in acidic solution.[BMBIm]Br compounds showed good protection performance in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution due to formation of an inhibitive film on the steel surface. A probable inhibitive mechanism is proposed through the viewpoint of adsorption theory.

## 2. Experimental

## 2.1. Material preparation

Electrochemical measurements were carried out in a three-electrode type cell with separate compartments for the reference electrode (Hg/HgCl), and the counter electrode was platinum (Pt) plate. Electrochemical studies were performed on mild steel specimens with weight percentage composition as follows: mild steel specimens of composition C = 0.08%, P = 0.07%, Si = 0%, S = 0%, Mn = 0.41%, and balance Fe. The dimension of coupons used for the experiment is 1 cm × 1 cm × 1 cm (L×B×Th). Prior to the commencement of the electrochemical experiments, the surface of the specimens was polished using a silicon carbide emery paper (100,250,400,600, 1000, 1200,1500 grade), washed thoroughly with double distilled water and dried on a clean tissue paper. At the end of the test, the specimens were carefully washed with benzene and acetone.

## 2.2. Chemical synthesis of investigated inhibitors

## 2.2.1. Synthesis of imidazolium ionic liquids 3-Butyl-1-methyl-1*H*-benzo (d)-imidazol-3-ium bromide [BMBIm] Br

Methyl imidazole and toluene were purchased from Sigma-Aldrich. Inhibitor was synthesized by mixing  $0 \cdot 1$  M of methylimidazole,  $0 \cdot 1$  M of 4-nitrobenzylbromide and 30 ml of toluene (Scheme 1) in a three-necked flask, which was provided with a magnetic stirrer, reflux condenser and thermometer. The reaction mixture was refluxed up to 110 °C for 24 h [26]. The reaction mixture forms two layers. The organic layer was extracted with toluene (3 × 30 ml). The solvent was

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evaporated in vacuum, and the product viz., [BMBIm]Br, ionic liquid was obtained with molecular weight of 268.06. The conversion of the crude product was checked by thin layer chromatography.



Scheme 1. Synthetic route of [BMBIm]Br.

## 2.3. Preparation of H<sub>2</sub>SO<sub>4</sub> solution

The analytical grade 98%  $H_2SO_4$  with molecular weight of 98.08 g/mole was used for preparing the acid electrolyte. The acid was exactly diluted with double distilled water to prepare 0.5M  $H_2SO_4$  solution. For each set of experiment freshly prepared 0.5 M  $H_2SO_4$  solutions were used to avoid effect of any contamination.

## 2.4. Electrochemical methods

Polarization curves and electrochemical impedance records were analyzed using electrochemical analyzer CHI 760C (CH Instrument Inc, USA). Potentiodynamic polarization and electrochemical impedance spectroscopy were performed using electrochemical analyzer CHI 760C (CH Instrument Inc, USA).

## 2.5. Surface analysis : SEM, AFM and EDX Spectroscopy

The surface morphology of the mild steel samples after immersion in the blank and inhibited solutions was observed by scanning electron microscope (SEM –JSM-6610 LV) and atomic force microscope (Nanosurf Naio) while the chemical composition of the surface was characterized by energy dispersive X-ray spectroscopy (scanning electron microscope (SEM –JSM-6610 LV).

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## 2.6. Computational methods

All calculations were done by using the package Hyperchem Pro 8.0.6 [27]. The molecular structure optimization was performed by using AM 1 (Austin model 1) semi-empirical method. Energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the energy gap between  $E_{LUMO}$  and  $E_{HOMO}$  ( $\Delta E = E_{LUMO}-E_{HOMO}$ ), dipole moment (µ), and other parameters were obtained from the theoretical studies for [BMBIm]Br.

## 3. Results and discussion:-

## 3.1 Synthesis

Methodology similar to previously reported procedure for the preparation of ionic liquids. Reflux of 1-Methylbenzimidazole with 1-Bromobutane in 30 ml of toluene at 110°C for 24 h gave IILs as viscous oil in good yields as shown in scheme 1. IILs were characterised by IR, <sup>1</sup>H & <sup>13</sup>C NMR spectroscopy. Analytical data of IILs corroborated well with their respective formulations.

## 3-Butyl-1-methyl-1H-benzo-imidazol-3-ium bromide [BMBIm]Br.

IR (neat, cm-1):n = 3408, 3095, 2829, 2230, 1567, 1516, 1450, 1419, 1285, 1234, 1161, 1108, 1081, 1024, 915, 823, 746, 661, 617; 1H NMR (400 MHz, CDCI3): δ 9.32 (s, 1H),8.26 (d, J = 8.4 Hz, 2H), 7.84(d, J = 1.5 Hz, 1H), 7.77 (d, J = 1.5 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 5.63 (s, 2H), 2.87 (s, 3H); 13C NMR (400 MHz, CDCI3): δ 141.9, 131.9, 130.9, 127.2, 113.0, 112.9, 47.4, 34.1, 31.1, 19.7, 13.4.

## 3.1. Open circuit potential (OCP)

The measurement of OCP is mandatory for all the corrosion studies as the electrochemical techniques like EIS operates at OCP; and the potentiodynamic polarization is carried out by drifting the system away from its equilibrium state. In both the cases OCP serves a significant role which if not attained, the results of electrochemical analyses would be affected. The freshly polished

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composite surface was dipped in the electrolyte to ensure the attainment of steady state. The variation of electrode potential with time was recorded. . The variation of electrode potential with time was recorded. It may be observed that initially, the potential changes up to a certain value which is called the induction time. On visual inspection of the electrode surface, a dull layer could be observed. This dull layer could be attributed to the surface deposition of the corrosion product or the oxide layer. After the initial induction period, the potential attains steady state implying an attainment of dynamic equilibrium between the surface film deposition and dissolution of the underlying metal by the breakdown or dissolution of the surface film. The corrosion inhibition effect of IL was investigated using open circuit potential (OCP), Tafel plots and A.C. impedance methods. OCP values in the presence of IL shifted to more positive potential with time compared to those of acid solution(Table1). For example, the steady state value of OCP for mild steel in blank solution was -465 mV whereas, in the presence of inhibitor it shifted toward the positive direction to  $-490 \pm 1$  mV. Thus, the shift in the steady state value of OCP in the presence of inhibitor was about 10 mV. This slight OCP displacement ( $\sim$ 10 mV) in the presence of inhibitor suggests that [BMBIm]Br act as mixed-type corrosion inhibitors. As it is known that only when change in OCP value is more than 85 mV it can be recognized as a classification evidence of a compound as an anodic or a cathodic type inhibitor [28]. On attaining the OCP, EIS and potentiodynamic polarization measurements were carried out.

## 3.2. Polarization studies

Fig.1 shows the polarization curves for [BMBIm]Br in 0.5 M  $H_2SO_4$  without and with various concentrations of [BMBIm]Br, at 298 °C. The presence of inhibitor causes a prominent decrease in the corrosion rate i.e. shifts both anodic and cathodic curves to lower values of current densities. Namely, both cathodic and anodic reactions of [BMBIm]Br electrode corrosion are drastically inhibited by [BMBIm]Br, in 0.5 M  $H_2SO_4$ . Values of corrosion current densities ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ), cathodic Tafel slope ( $b_c$ ), anodic Tafel slope ( $b_a$ ), and inhibition efficiency are listed in Table 1. Clearly, lcorr decreases prominently while  $\eta$  increases with the increase of inhibitor concentration, and the maximum is up to 99.62%. Ecorr slightly shifts to positive and ba changes in the presence of [BMBIm]Br, which indicates that inhibitor molecules are more adsorbed on the anodic sites resulting in an inhibition of the anodic reactions. Tafel slope of bc does not change upon addition of [BMBIm]Br, which indicates that the presence of [BMBIm]Br, does not affect the mechanism of hydrogen reaction. Generally, if the displacement in Ecorr is >85 mV with respect to

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 $E_{corr}$  in uninhibited solution, the inhibitor can be seen as a cathodic or anodic type . In our study the maximum displacement is 32 mV, which indicates that [BMBIm]Br, acts as a mixed-type inhibitor[28].

## 3.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy provides information about the kinetics of mild steel corrosion at  $10^{-2}$  M in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium and about the surface properties of the mild steel in the absence and in presence of [BMBIm]Br. Fig. 2 shows the Nyquist plots represented by imperfect semicircles for the impedance data of mild steel at  $10^{-2}$  M in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium in the absence and presence of [BMBIm]Br, at 298 k. The charge transfer resistance (Rct) and double layer capacitance (CdI) values were obtained from Nyquist plots and summarized in the Table 2. The diameter of imperfect semicircles (Rct) in Nyquist plots increased on increasing the concentration [BMBIm]Br which implied the formation of adsorption film and indicated the strengthening of inhibitor film. it was found to be same in the presence and absence of IL and composed of one semicircle indicating that a charge transfer process at the mild steel is the rate determining step. However, deviation from perfect semicircle indicates some in homogeneity or roughness of the mild steel surface [28].

The Bode phase angle plots (Fig. 2b) show single maximum (one time constant) at intermediate frequencies, broadening of this maximum in the presence of inhibitors accounts for the formation of a protective layer on the electrode surface. Moreover, there is only one phase maximum in Bode plot (Fig.2b) for both inhibitors, which indicates only one relaxation process, which would be the charge transfer process, taking place at the metal–electrolyte interface

## 3.4. Adsorption isotherm

The adsorption of organic molecules provides information about the interaction among the adsorbed molecules themselves as well as their interaction with the electrode surface. The degree of surface coverage ( $\theta$ ) for different concentrations of inhibitor molecules in 0.5 M H<sub>2</sub>SO<sub>4</sub> was calculated from galvanostatic polarization studies () values were calculated from the equation:

1

where  $I_{corr}$  (Inhibitor) is the corrosion current density in the presence of inhibitors and  $I_{corr}$  (Acid) is the corrosion current density in the absence of inhibitor in the solution.

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The equation that fits our results is that due to Langmuir isotherm and is given by the general equation :

2

where C is the inhibitor concentration,  $K_{ads}$  is the adsorptive equilibrium constant and  $\theta$  is the surface coverage. The surface coverage ( $\theta$ ) was tested graphically for fitting a suitable adsorption isotherm as indicated in Fig. 7. Plotting C/ $\theta$  vs. C yielded a straight line with a regression coefficient (R<sup>2</sup>) higher than 0.999 and a slope closed to 1. This suggests that the experimental data are well described by Langmuir adsorption isotherm.

The values of the standard free energy of adsorption ( $\Delta G_{\circ}$  ads) equation (3) . are also presented in Table 3. The negative value of  $\Delta G_{\circ}$  ads ensures the spontaneity of the adsorption process [29]:

$$\Delta G^{0}_{ads} = -RT \ln(55.5 \text{ K})$$
[3]

where R is the gas constant and T is the absolute temperature (K). The value of 55.5 is the molar concentration of water in solution.

The calculated value of  $\Delta G^{\circ}$  ads, obtained from the method employed was found to be less negative than e 40 kJ mol1. It is well known that the absolute values of  $\Delta G^{\circ}_{ads}$  on the order of -20 kJ/mol or lower indicate physisorption; those on the order of -40 kJ/mol or higher involve charge sharing or a transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond. Accordingly, the values of  $\Delta G^{\circ}_{ads}$  obtained in the present study indicate that the adsorption mechanism of these inhibitors on steel involves two types of interactions, chemisorption and physisorption. Indeed, due to the strong adsorption of water molecules onto the surface of mild steel, one may assume that adsorption occurs first due to the physical forces. The removal of water molecules from the surface is accompanied by a chemical interaction between the metal surface and the adsorbate, which becomes chemisorption.

Four types of adsorption may take place involving [BMBIm] Br molecules on the mild steel -solution interface:

- (i) Electrostatic attraction between charged molecules and the charged metal,
- (ii) Interaction of unshared electron pairs in the molecule with the metal,

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- (iii) Interaction of  $\pi$ -electrons with the metal,
- (iv) A combination of the above.

## 3.5. Morpholgical studies:-

## 3.5.1. Scanning Electron Microscopy Studies:

The surface morphology of mild steel samples immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 4 hours in the absence and presence of 10<sup>-2</sup> M of [BMBIm]Br was studied by scanning electron microscopy (SEM). The solutions were not degassed. Figure 3 shows the surface morphology of mild steel specimens (a) before and (b) after being immersed in corrosive solution. Figure 3(b) reveals that the surface was strongly damaged in the absence of inhibitors. The presence of bromide ions and dissolved oxygen contributes to the oxidation of the metal. Figure 3(c) shows SEM image of the surface of specimens after immersion for the same time interval in corrosive solution additionally containing 10<sup>-2</sup> M of [BMBIm]Br. However, in these conditions, the film precipitates on the surface of mild steel (Figure 3(c)). The SEM photographs show that it does not cover tightly the surface and hence does not protect the mild steel surface to an sufficient amount. oxygen, and water penetrate the protective film through pores, flaws, or other weak spots what results in further corrosion of mild steel. The results of the action of aggressive environment were visible after the removal of protective layer from the surface of mild steel. It well adhere to surface of the metal, and removal of protective film was difficult enough. In this aim, ultrasonic water baths were used. The sample was shaken in diluted sulphuric acid and rinsed in propanol.

#### 3.5.2. Energy dispersive X-ray analysis (EDX) technique:

Energy dispersive X-ray analysis (EDX) technique was employed in order to get information about the composition of the surface of the mild steel sample[30] in the absence and presence of inhibitors in 0.5 M  $H_2SO_4$  solution. The results of EDX spectra are shown in Fig. 4 (a–d). The percentage atomic content of various elements of the polished, uninhibited and inhibited mild steel surface determined by EDX is shown in figure. The percentage atomic content of Fe for mild steel immersed in 0.5 M  $H_2SO_4$ 

#### 3.5.3. AFM Studies:

AFM was used for further study about the surface morphology on MS surface. Fig.5(a–d) shows the different 3D images of MS in different conditions. Fig 5 (b) shows the corroded MS surface with average roughness 644 nm. The higher surface roughness of MS exposed to blank solution shows a bumpy structure with a large number of ups and downs due to acid attack. From Fig. 5 (b–d) it can be observed that on adding inhibitor in acid solution the surface morphology of MS changed due to formation of adsorbed protective layer [31] which can be understood by a decrease in average surface roughness from 644 to 182 nm.

#### 3.6 Quantum Chemical Calculation:

 $E_{HOMO}$  measures the tendency of inhibitor towards the donation of electrons to the vacant d-orbitals of iron metal surface. The higher the  $E_{HOMO}$  of the inhibitor, the better is its ability to donate electrons to the acceptor molecule with low lying empty orbital and better will be the inhibition efficiency. The frontier molecular orbital indicates that for IL concerned inhibitor molecule the electrons are spread over the entire molecule. The adsorption ability of the molecule on the metal surface is related to their frontier molecular orbital i.e.; highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) electron densities and energies [32]. The high electron densities on those four -C=N bonds of imidazole rings will help for a parallel or flat disposition of the inhibitor molecules on metal surface, which in turn will help in the adsorption of the inhibitor molecules on metal surfaces. This was reflected from enhanced inhibition efficiencies. Quantum chemical parameters like  $E_{HOMO}$ ,  $E_{LUMO}$ , energy gap ( $\Delta E$ ), electronegativity ( $\chi$ ), softness (S) and fraction of electron transferred ( $\Delta N$ ) are given in Table 5 and these parameters are responsible for the reactivity of the IL as efficient corrosion inhibitor.  $E_{LUMO}$  depicts the ability of a molecule to accept electrons. The lower is the  $E_{LUMO}$  value, the higher will be the possibility of the inhibitor to accept electrons from the metal d-orbital.

#### **Conclusions and future trends:**

The electrochemical measurements demonstrate that Inhibition efficiency increased with increase in concentration of IL and inhibitor acted as a mixed-type inhibitor to retard simultaneously the anodic and cathodic processes through the forming of adsorption film on steel surface according to

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Langmuir adsorption isotherm. The inhibition efficiency increases with increase in concentration and decreases with increase in temperature and acting as mixed type of inhibitors as indicated by insignificant change in the E<sub>corr</sub> values. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies reveal that the extent of corrosion is lesser in higher concentrations as compared to the lower concentrations. These results are in good agreement with the ones obtained from the earlier electrochemical techniques. Lifetime of orthopedic implants is a key issue for patient life and health issues all over the world. Metals used for implants were specifically submitted to friction/fretting corrosion processes; with a specific attention on the main differences between these two types of degradations. Moreover the synergistic approach, contribution of wear on corrosion and vice versa is relevant for understanding the role of each mode of degradations. Theoretical and practical issues are related to understanding these phenomena and revealing insights for the future opportunities and challenges.

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Figure 1. Polarization curves for mild steel in absence and presence of different concentration of [BMBIm]Br. at 298 K in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



Figure 2. [a]. Nyquist plot for different concentration of [BMBIm]Br. [b]. Bode plot (log f vs. log|Z|) in  $0.5 \text{ M H}_2\text{SO}_4$  without and with different concentrations of [BMBIm]Br.

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Figure 3. SEM images of mild steel surfaces: (a) abraded, (b) in absence of [BMBIm]Br and in the presence of (c) 10<sup>-2</sup> M of [BMBIm]Br (d) 10<sup>-5</sup> M of [BMBIm]Br



Figure 4. EDX images of mild steel surfaces: (a) abraded, (b) in absence of [BMBIm]Br and in the presence of (c) 10<sup>-2</sup> M of [BMBIm]Br (d) 10<sup>-5</sup> M of [BMBIm]Br



Figure: 5. AFM micrographs of the MS surface: (a) abraded MS; (b) blank in 0.5 M H<sub>2</sub>SO<sub>4</sub>; (c) with [BMBIm]Br (10<sup>-2</sup> M) in H<sub>2</sub>SO<sub>4</sub>; (d) with [BMBIm]Br (10<sup>-5</sup>) M in H<sub>2</sub>SO<sub>4</sub>.



Figure 6. Electronic properties of [BMBIm]Br (a) Opimized structure (b) 3-D Mapped Isosurface (c)Electrostatic Potential with 3-D Mapped Isosurface (d) Total Charge Density with 3-D Mapped Isosurface (e) HOMO orbital density (f) LUMO orbital density Atom legend: white = H; gray = C; red = O; blue = N.



Figure 7. (a) Langmuir isotherm plots for the adsorption of [BMBIm] Br on mild steel surface in 0.5 M  $H_2SO$ 

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## Table 1.

Electrochemical kinetic parameters and inhibition efficiencies, IE (%), associated with polarization measurements (Tafel polarization) mild s steel in 0.5 M  $H_2SO_4$  solution containing various concentrations of [BMBIm]Br at 298 K

Conc.	(-)E <sub>corr</sub>	b <sub>a</sub>	-b <sub>c</sub>	I <sub>corr</sub>	θ	$\eta_{GPS}$
(171)	(mv)	(mv/dec)	(mv/dec)	(µA/cm²)		(%)
0	465	141.60	164.20	008805.00		
0.00001	453	084.04	100.46	000124.90	0.85	85.81
0.0001	493	096.61	110.95	000589.40	0.93	93.3
0.001	497	060.94	107.20	000084.43	0.99	99.04
0.01	490	134.46	095.43	000033.35	0.99	99.62
	Conc. (M) 0 0.00001 0.0001 0.001 0.001	Conc.         (-)E <sub>corr</sub> (M)         (mV)           0         465           0.00001         453           0.0001         493           0.001         497           0.01         490	$\begin{array}{c cccc} Conc. & (-)E_{corr} & b_a \\ \hline (M) & (mV) & (mV/dec) \\ \hline 0 & 465 & 141.60 \\ 0.00001 & 453 & 084.04 \\ 0.0001 & 493 & 096.61 \\ 0.001 & 497 & 060.94 \\ 0.01 & 490 & 134.46 \\ \hline \end{array}$	$\begin{array}{c ccccc} Conc. & (-)E_{corr} & b_a & -b_c \\ \hline (M) & (mV) & (mV/dec) & (mV/dec) \\ \hline 0 & 465 & 141.60 & 164.20 \\ 0.0001 & 453 & 084.04 & 100.46 \\ 0.0001 & 493 & 096.61 & 110.95 \\ 0.001 & 497 & 060.94 & 107.20 \\ 0.01 & 490 & 134.46 & 095.43 \\ \end{array}$	$\begin{array}{c cccccc} Conc. & (-)E_{corr} & b_a & -b_c & I_{corr} \\ \hline (M) & (mV) & (mV/dec) & (mV/dec) & (\muA/cm^2) \\ \hline \\ 0 & 465 & 141.60 & 164.20 & 008805.00 \\ 0.0001 & 453 & 084.04 & 100.46 & 000124.90 \\ 0.0001 & 493 & 096.61 & 110.95 & 000589.40 \\ 0.001 & 497 & 060.94 & 107.20 & 000084.43 \\ 0.01 & 490 & 134.46 & 095.43 & 000033.35 \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

## Table 2

Electrochemical kinetic parameters obtained by EIS technique for mild steel in aerated 0.5 M  $H_2SO_4$  solutions containing various concentrations of [BMBIm]Br at 298 K

Conc. (M)	R <sub>p</sub> (Ω cm <sup>-2</sup> )	R₅ (Ω cm⁻²)	F <sub>max</sub> (Hz)	R <sub>ct</sub> (Ω cm <sup>-2</sup> )	C <sub>dl</sub> (µF cm <sup>−2</sup> )	η <sub>ΕΙS</sub> (%)
[BMBIm]Br	X /	· · · · ·			u ,	
0.00001	020.48	0.78	11.91	019.69	0680.00	92.78
0.00010	037.12	1.33	08.07	035.78	0550.00	96.03
0.00100	183.56	0.64	04.54	182.92	0190.00	99.22
0.01000	463.82	0.74	02.55	463.07	0130.00	99.69

#### Table 3

Adsorption thermodynamic parameters of [BMBIm]Br at 298 K temperature.

Inhibitors	Log K <sub>ads</sub>	- $\Delta G^{o}_{ads}$	$\Delta H^{o}_{ads}$	$\Delta {f S^o}_{ads}$	
		KJ/mol	KJ/mol	J/mol-K	
[BMBIm]Br	4.31	40.24	19.21	-199.50	

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## Table 4

Roughness parameters calculated using atomic force microscope (Nanosurf Naio) of [BMBIm]Br

Conc.	Ra	Rs
(M)	(nm)	
MS in acidic medium	644.91	532.82
Plain MS	18.19	49.02
0.00001	330.13	646.04
0.01000	182.27	444.83

## Table 5

Optimized Parameters Calculated using Quantum Chemical Calculations of [BMBIm]Br

Quantum chemical parameters	[BMBIm]Br	
Е <sub>номо</sub> (eV)	-6.37	
E <sub>LUMO</sub> (eV)	-0.05	
ΔE (eV)	6.32	
μ (Debye)	4.41	
Heat of formation	-86.21	
$(KJ \Pi U I^{*})$	6.27	
	0.37	
Electron Affinity, A (eV)	0.05	
Hardness (η)	3.16	
Electronegativity ( $\chi$ )	-3.16	
Fraction of electron ( $\Delta N$ )	-1.60	
%IE	99.62	