Research Articles

Anti-Corrosion Properties of benzothiazole Derivatives for Mild Steel in 1M H_2SO_4 Solution

V. Hemapriya[*], K. Parameswari and S. Chitra

Department of Chemistry, PSGR Krishnammal College for Women, Coimbatore – 4, Tamil Nadu, India

Abstract

The corrosion inhibition performance of benzothiazole derivatives namely, 2-phenylbenzothiazole(PBT), 2-(4-methoxy-phenyl)benzothiazole(MPB) and 2-(3,4,5-trimethoxy-phenyl)benzothiazole(TPB) on mild steel in 1M H_2SO_4 has been studied by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. The experimental results showed that the inhibition efficiency increases with increase in inhibitor concentration but decreases with increasing temperature. The inhibition has been assumed to occur via adsorption of inhibitors on mild steel surface. This is supported by the results obtained from scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. Adsorption of inhibitors on mild steel surface follows Langmuir adsorption isotherm. The activation energy and free energy of adsorption for the inhibition reaction support the mechanism of physical adsorption. Potentiodynamic polarization measurements indicate that the studied benzothiazole derivatives act as mixed inhibitors. Quantum chemical calculations have been performed and quantum chemical indices were calculated to supplement the experimental results.

Keywords: benzothiazole, corrosion, adsorption, polarisation, DFT
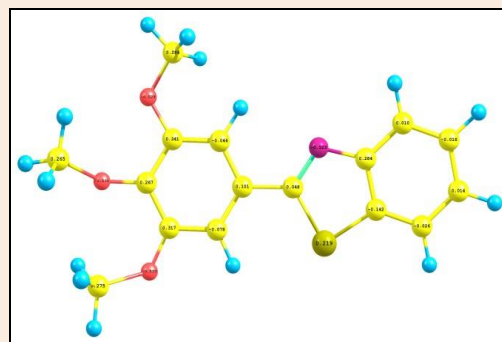
*Correspondence
V. Hemapriya,
Email: hemahimma@gmail.com

Introduction

Mild steel finds many applications in industries due to its easy availability, fabrication, good tensile strength and low cost besides other desirable qualities. The major problem associated with mild steel is its dissolution when it comes in contact with acid solutions during cleaning, descaling, acid storage and various other chemical processes. This is eliminated by the use of inhibitors. Organic compounds containing sulphur, nitrogen, oxygen, polar functional groups and conjugated double bonds are proven as potential corrosion inhibitors[1-2].

Benzothiazoles are an extremely important class of compounds that occur widely in biologically active natural products as well as in the marketed drugs. The benzothiazole nucleus is present in compounds that possess interesting biological activities such as antitumor, antimicrobial, anthelmintic, antileishmanial, anticonvulsant and anti-inflammatory. They also found application in industry as antioxidants and vulcanization accelerators. An insight of previous work reveal that only limited work has been reported on the corrosion inhibition of 2phenyl benzothiazole derivatives in acid media. The present study deals with the study of corrosion inhibition capacity and mechanism of inhibition of 2-(substituted phenyl) benzothiazoles (PBT, MPB &TPB).

Experimental work

Material: Mild steel specimens(C=0.079%, P=0.025%, Mn=0.018%, S=0.021% and the rest Fe) of dimensions 3 cm X 1 cm x 0.05 cm were polished to mirror finish and degreased with trichloro ethylene and used for the weight loss

and surface examination studies. For electrochemical studies mild steel rod with exposed area of 0.785cm^2 was used. The inhibitors used for the study were prepared by the reported procedure [3] and characterised by FTIR spectra.

Weight loss method

Pretreated and weighed mild steel specimens were immersed in 1M H$_2$SO$_4$ containing various concentrations of inhibitors over a period of 3 hrs at 30± 1° C. The specimens were reweighed and from the mass loss corrosion rate and inhibition efficiency were calculated. To find the effect of temperature on inhibition efficiency mass loss experiments were carried out in the temperature range 30-60° C.

Electrochemical measurements

Electrochemical measurements were carried out using a conventional three electrode cell assembly with Ivium compactstat instrument. Anodic and cathodic polarization curves were recorded in the potential range of-200mV to +200mV, at a scan rate of 1 mVs^{-1}. The AC impedance measurements were performed in the frequency range from 0.01Hz to 10KHz with a signal amplitude of 25 mV. Nyquist plots were drawn and the inhibition efficiency was calculated using charge transfer resistance.

Surface Examination Studies

Surface morphology of mild steel specimens immersed in inhibited and uninhibited solutions were examined using scanning electron microscopy (SEM) Fourier transform infrared spectroscopy, energy dispersive X-ray (EDX) technique and atomic force microscopy studies (AFM).

Quantum chemical studies

Quantum chemical analysis was performed using DFT method at B3LYP/6-31G(*d,p*) level of Gaussian 09 programme. Total energy, dipole moment, charge density, energies of highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital and the band gap were examined to evaluate the corrosion inhibition efficiency of the inhibitors.

Results and Discussion

Weight loss measurements

Table 1 Inhibition efficiency at various concentrations of inhibitors for the corrosion of mild steel in 1M H$_2$SO$_4$ obtained by weight loss measurements at 30±1°C

Inhibitor	PBT		MPB		TPB	
Concentration (mM)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
0.01	46197	54.94	60438	41.05	7104	93.07
0.02	15420	84.95	41927	59.10	2421	97.63
0.04	7550	92.63	15547	84.83	1146	98.88
0.06	4524	95.58	6499	93.66	828	99.19
0.08	2676	97.38	4332	95.77	541	99.47
0.1	2580	97.48	1497	98.53	414	99.59

Corrosion parameters such as corrosion rate and inhibition efficiency of the inhibitors are given in **Table 1**. The corrosion rate of mild steel decreases and inhibition efficiency of the inhibitor increases with increase in concentration of the inhibitor due to the sufficient adsorption of inhibitor and wider coverage of the steel surface.

Effect of temperature

The effect of temperature on the inhibition efficiency of the inhibitors is presented in **Figure 1**. Inhibition efficiency decreases with increase in temperature. Energy of activation calculated from Arrhenius slopes [**Figure 2**] indicates physical adsorption. Negative ΔG values [**Table 2**] suggest spontaneity of the adsorption process and the values are less than -40kJ/mole confirming physical adsorption [4]. ΔH values obtained from the transition state plot [**Figure 3**] show the thermodynamic nature of metal dissolution. The positive ΔS values indicate the less orderliness of the transition state of adsorption process.
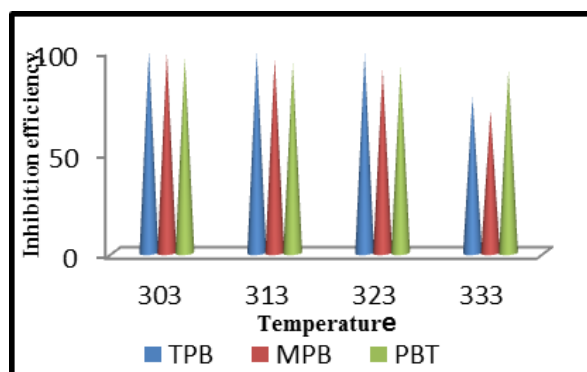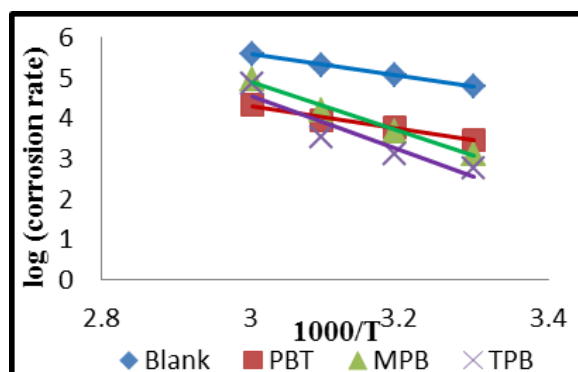

Figure 1 Effect of temperature on IE

Figure 2 Arrhenius plot

Table 2 Activation energy (Ea) and free energy of adsorption (ΔG^0_{ads}) for the corrosion of mild steel in IM H_2SO_4 at 0.1mM concentration of the inhibitor

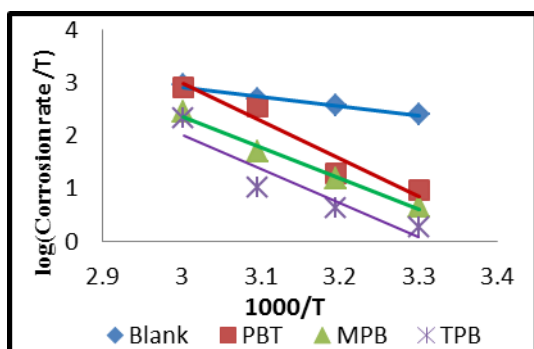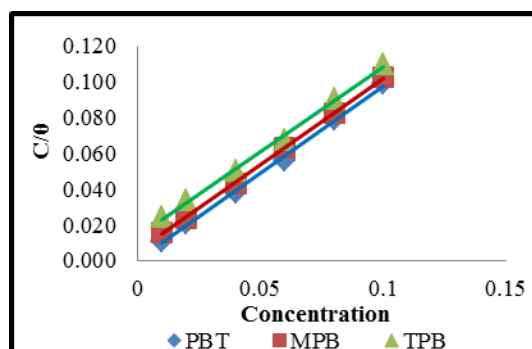| Inhibitor	Ea (kj)	ΔG°_{ads} (KJ)				ΔS (jmol^{-1})	ΔH (Kjmol^{-1})
		303 K	313 K	323 K	333 K		
Blank	50.92	-	-	-	-	-4.67	14.93
2-PBT	54.79	-24.18	-23.89	-24.56	-24.56	8.85	22.59
MPB	116.38	-26.14	-24.5	-22.9	-19.82	94.07	49.38
TPB	127.64	-28.3	-27.99	-27.37	-20.83	105.93	54.28

Figure 3 Transition state plot

Figure 4 Langmuir plot

Adsorption isotherm

The surface coverage values obtained from weight loss measurements were tested by fitting various adsorption isotherms. The best fit was found to be with Langmuir, Flory-Huggins and El-awady kinetic thermodynamic model [**Figure 4-6**]. The adsorption of the inhibitors on mild steel surface as a monolayer is confirmed by Langmuir adsorption isotherm. Florry –Huggins isotherm can be expressed as

$$Kc = \theta/e^{(x-1)}(1-\theta)^x$$

Where x is the number of adsorbed water molecules replaced by one molecule of organic adsorbate, c is the inhibitor concentration in the bulk of the solution. K is the equilibrium (the binding) constant of adsorption process, the magnitude of K is directly proportional to the inhibition efficiency. The values of x >1 imply the formation of multilayer of the inhibitor on the metal surface and x less than one mean that the given inhibitor molecule will occupy more than one active site [5]. According to the kinetic – thermodynamic model of El-awady

$$\log(\theta/1\text{-}\theta) = \log K'^{(1/y)}$$

$$K=K'^{(1/y)}$$

Where, 1/y represents the number of active sites of the surface occupied by one inhibitor molecule. Value of 1/y less than unity implies the formation of multilayer of the inhibitor on the surface of the metal. Values of 1/y greater than unity indicate that a given inhibitor molecule will occupy more than one active site [6].The adsorption parameters obtained from Flory Huggins isotherm and the kinetic model are given in **Table 3**. The values of 1/y were found to be greater than unity indicating that each inhibitor occupies more than one active site. This is supported by the values of x which are less than one.
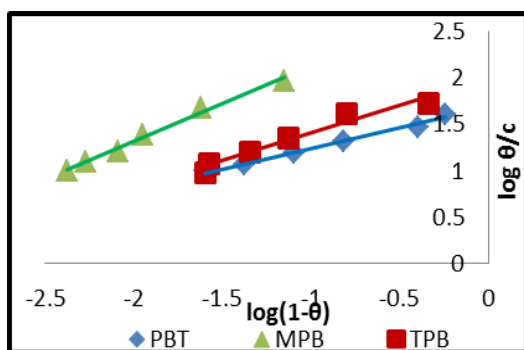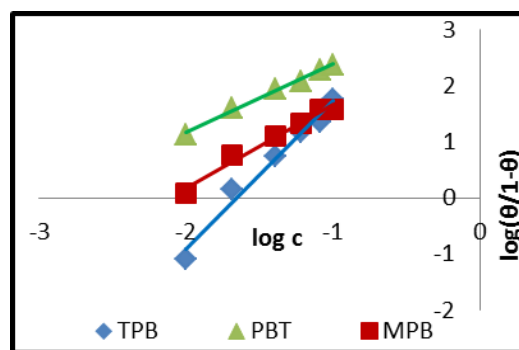

Figure 5 Flory-Huggins adsorption isotherm plots

Figure 6 El-awady kinetic model

Table 3 Adsorption kinetic parameters for the inhibitors on mild steel surface in 1M H_2SO_4

Inhibitor	El-awady(kinetic model)		Flory-Huggins model	
	1/y	K	X	K
PBT	1.49	3.15	0.59	2.00
MPB	2.67	4.41	0.44	1.68
TPB	1.22	3.60	0.80	2.93

Potentiodynamic polarization studies

Figure 7 shows the Tafel curves for mild steel in the presence and absence of various concentrations of inhibitor in 1M H_2SO_4. The values of electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and Tafel constants (b_a and b_c) obtained from cathodic and anodic curves listed in **Table 4** suggest that the inhibitors are mixed type and inhibit corrosion by blocking the active sites.

Table 4 Corrosion parameters for mild steel at selected concentrations of the inhibitors in IM H_2SO_4 by potentiodynamic polarization method at 30 ± 1^oC

Name of the Inhibitor	Inhibitor Concentration mM	Tafel Slopes (mV/decade)		E_{corr} (mV)	I_{corr} ($\mu A/Cm^2$)	Inhibition efficiency (%)
		b_a	b_c			
	BLANK	69	121	-473.6	3108	
	0.01	72	127	-493.5	1622	47.81
	0.06	52	140	-490.3	924	70.27
PBT	0.1	36	146	-470.0	526	83.08
	0.01	46	132	-481.1	1055	66.06
	0.06	33	164	-447.1	652	79.02
MPB	0.1	19	160	-422.0	401	87.10
	0.01	42	156	-473.5	1012	68.73
	0.06	40	189	-476.5	796	74.39
TPB	0.1	24	98	-450.8	262	91.57

AC impedance measurements

The Nyquist representation of impedance behavior of mild steel in 1M H_2SO_4 with and without inhibitor (MPB) is depicted in **Figure 8.** Semicircular nature of Nyquist plots suggests that a charge transfer process controls the corrosion of mild steel in 1M sulphuric acid. The impedance parameters calculated from Nyquist plots are given in **Table 5**. It is observed that the charge transfer resistance (R_{ct}) values increased and the double layer capacitance (C_{dl}) values decreased with increase in concentration of the inhibitor.
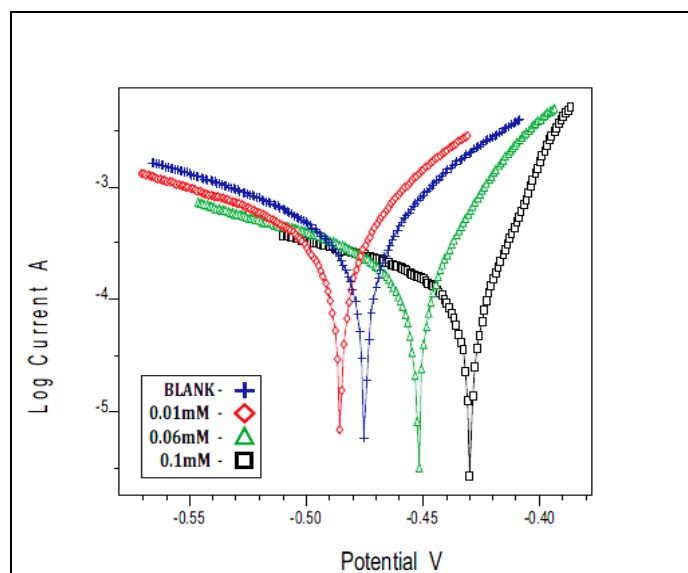

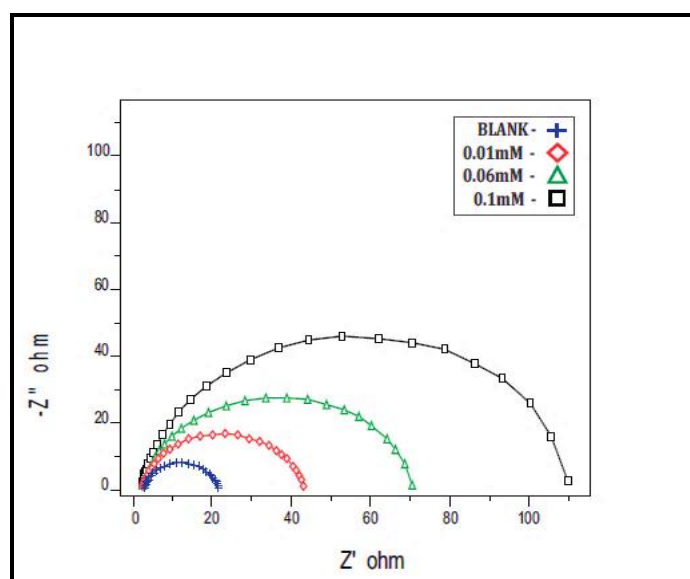**Figure 7** Tafel slope for mild steel in the absence and presence of MPB

**Figure 8** AC impedance spectra for mild steel in the presence and absence of MPB 1M H_2SO_4

Table 5 AC Impedance parameters for mild steel at selected concentrations of the inhibitors in IM H_2SO_4

Inhibitor	Concentration Mm	R_t (ohm/cm^2)	C_{dl} ($\mu F/Cm^2$)	IE (%)
	BLANK	13.8	413.58	
	0.01	30.03	200.85	54.05
	0.06	41.05	159.63	66.38
PBT	0.1	48.75	129.62	71.69
	0.01	33.48	222.25	58.78
	0.06	57.28	135.61	75.91
MPB	0.1	94.5	115.41	85.40
	0.01	59.03	129.07	76.62
	0.06	88.6	100.97	84.42
TPB	0.1	122.16	69.71	88.70

Surface morphology studies

SEM Analysis

The formation of inhibitive adsorption film of the inhibitors on mild steel surface was confirmed by the SEM analysis. **Figure 9a** shows the effect of aggressive acidic solution whereas **Figure 9b** showed the adsorption of inhibitor molecules on the surface. The SEM images revealed that the metal surface immersed in 1M H_2SO_4 is rough and covered with corrosion products and appeared to have of pits and cavities whereas the specimens immersed in the inhibitor solutions are in better conditions with a smooth surface. This shows that the inhibitor molecules hinder the dissolution of mild steel by forming surface adsorbed layer and thereby decreasing the corrosion rate.

9a   9b
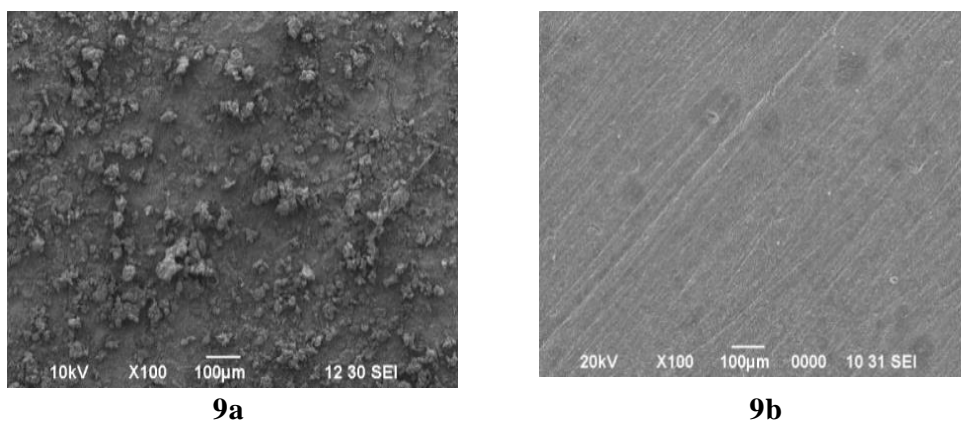
Figure 9 SEM micrograph of mild steel in the absence and presence of MPB

FTIR spectroscopy

To understand the mode of interaction of inhibitor molecules with the mild steel surface IR spectrum of the pure MPB is compared with the spectrum of film formed on the surface of metal specimen after weight loss studies. FT IR spectrum of pure (**Figure 10**) MPB shows peaks at 830 cm⁻¹, 1477 cm⁻¹ and 1599 cm⁻¹ characteristic of C-S, C-N and C=N. The spectrum of scratched sample from mild steel specimen immersed in 0.1mM MPB shows stretching vibrations at 742 cm⁻¹, 1470 cm⁻¹ and 1538 cm⁻¹ which may be due to C-S, C-N and benzothiazole moiety. These results suggest that the C=N & C-S groups of the thiazole ring must have been used for the adsorption of the inhibitors on the steel surface.
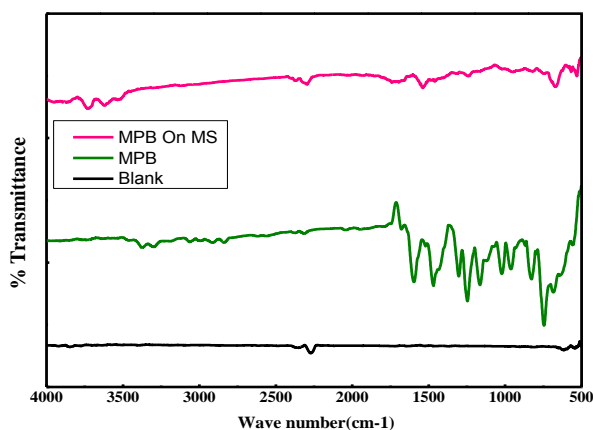

Figure 10 IR Spectra Quantum Chemical Calculations

Table 6 Calculated quantum chemical parameters of the inhibitors

Parameters	PBT	MPB	TPB
E_{HOMO} (eV)	-6.0398	-5.9547	-5.6586
E_{LUMO} (eV)	-1.5809	-1.5061	-1.4354
ΔE (eV)	4.4588	4.4485	4.2232
Dipole moment (Debye)	0.6561	1.7864	2.3562
IP (eV)	6.0398	5.9547	5.6586
EA (eV)	1.5809	1.5061	1.4354
Softness σ	0.4485	0.4495	0.4735
Electronegativity χ (eV)	3.8103	3.7304	3.547
Hardness η	2.2294	2.2243	2.1116
Total energy	-953.76	-1068.28	-1297.31
Molar volume (cm³/mol)	157.67	176.21	208.23
Transferred electrons fraction (ΔN)	0.7153	0.7349	0.817
$\Delta E_{back\ donation}$	-05573	-0.5560	-0.5279

To investigate the correlation between molecular structure of the inhibitors and their inhibition efficiency quantum chemical studies have been implemented for the compounds PBT and MPB. The quantum chemical parameters such as total energy, dipole moment, charge density, energies of highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals and the band gap were examined to evaluate the corrosion inhibition efficiency of the inhibitors and are listed in **Table 6**. The optimised geometries and the molecular orbital density distributions (HOMO and LUMO) are shown in **Figure 11**. E_{HOMO} is associated with electron donating ability of a molecule and E_{LUMO} is connected with the ability of the molecule to accept electrons [7]. Behpour et al [8] reported that higher values of E_{HOMO} facilitate adsorption by influencing the transport process through the adsorbed layer. The lower the value of E_{LUMO} high it is probable the molecules to accept electrons [9]. E_{HOMO} for the studied compounds follow the order TPB > MPB > PBT, which shows that TPB has highest tendency to donate electrons. This is in agreement with the experimental results. According to Gece et al [10] low values of energy gap ΔE will cause higher inhibition efficiency because excitation energy to remove an electron from the highest occupied orbital will be minimised. In the present study TPB has higher energy gap than MPB followed by PBT in agreement with the experimental results. According to Obi-Egbedi et al [11] that there is no definite correlation exists between dipole moment and inhibition efficiency. High ionization energy indicates high stability and chemical inertness and low ionization energy indicates high reactivity of the atoms and molecules [12]. The low ionization energy of TPB indicates its high inhibition efficiency.

Ebenso et al have reported that a compound with low global hardness and high softness value is expected to have higher inhibition efficiency [13]. TPB with softness value 0.4735 which is higher than PBT and MPB and shows higher inhibition efficiency.
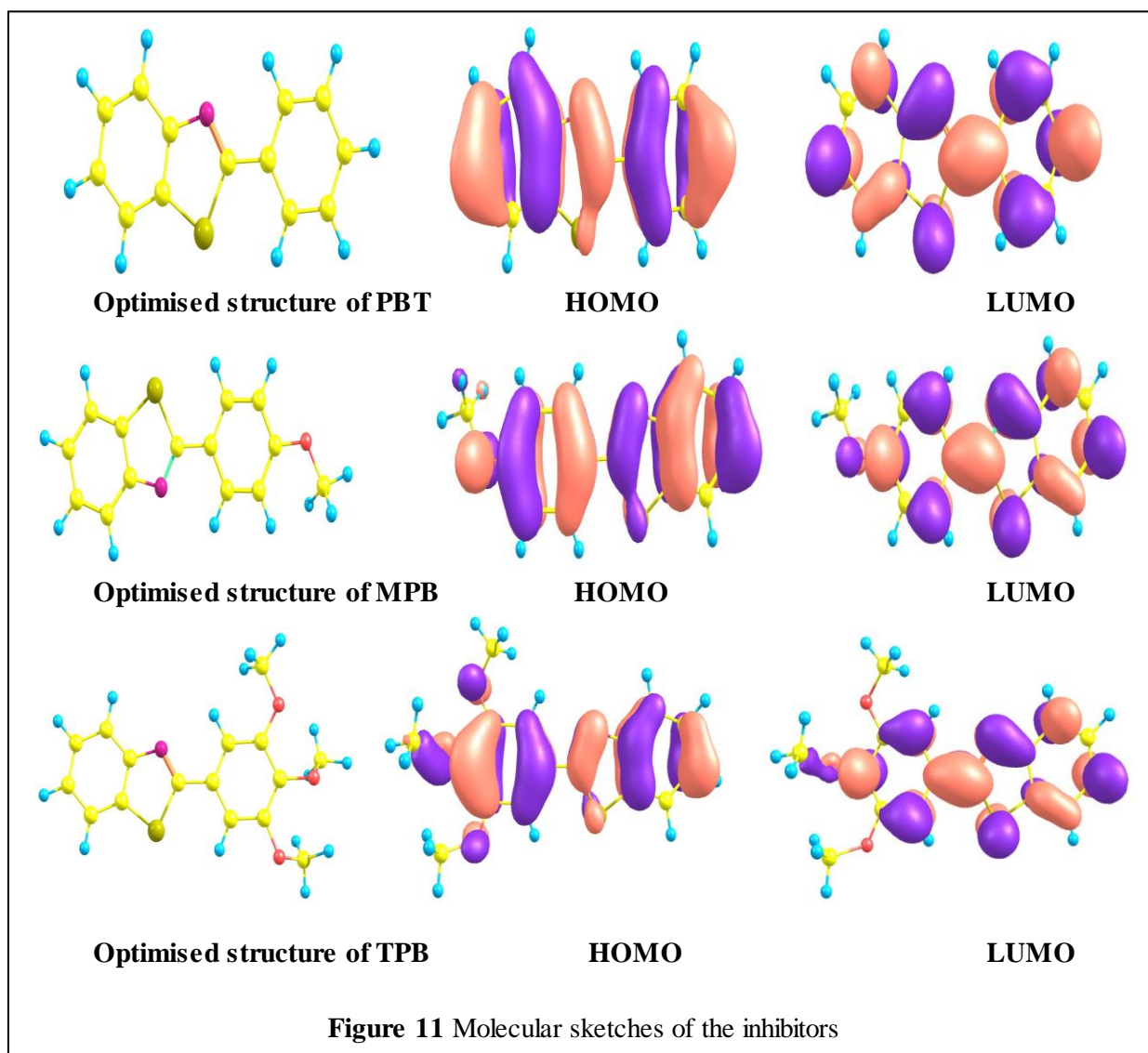
Molecular volume is an index of possible surface coverage of metal by the inhibitor. The larger the molecular volume, greater is the inhibition efficiency because of increased surface coverage. The large molecular volume of TPB indicates its higher protection efficiency.

Table 7 Mulliken charge densities

Atom numbering	Mulliken Charges		
	PBT	**MPB**	**TPB**
C1	0.015528	0.014793	0.013593
C2	-0.013845	-0.014615	-0.016008
C3	-0.024104	-0.025267	-0.025648
C4	0.014322	0.014854	0.009599
C5	-0.141321	-0.141115	-0.141860
C6	0.049876	0.281300	0.283895
C7	0.100604	0.046933	0.047896
C8	-0.027034	0.099955	0.100649
C9	0.029872	-0.035239	-0.077940
C10	-0.002846	-0.003684	-0.045601
C11	0.002318	-0.012997	0.316989
C12	0.014784	0.353671	0.341236
C13	-	-0.038301	0.266891
C14	-	0.272665	0.284129
C15	-	-	0.265003
C16	-	-	0.275344
N	-0.512071	-0.509650	-0.522951
S	0.212876	0.213367	0.218989
O1	-	-0.516671	-0.529292
O2	-	-	-0.531494
O3	-	-	-0.533417

These findings are compatible with the fraction of electrons transferred (ΔN) which indicates the tendency of a molecule to donate electrons. Greater the value of ΔN, greater is the tendency of the molecule to interact with the metal surface[14] (i.e., a greater tendency to adsorb on the metal surface). In the present study electron donating ability of the inhibitors increases in the order PBT< MPB < TPB which indicates that ΔN values correlate with inhibitor efficiency.

The Mulliken charge densities calculated from optimised geometry are given in Table 7. The data reveal that the thiazole nitrogen and most of the carbon atoms of inhibitor molecules carrying negative charges may be used for forming bond with positively charged metal atoms on the surface [15].

Optimised structure of PBT	HOMO	LUMO
Optimised structure of MPB	HOMO	LUMO
Optimised structure of TPB	HOMO	LUMO

Figure 11 Molecular sketches of the inhibitors

Mechanism of inhibition

Corrosion inhibition of mild steel in sulphuric acid solution by benzothiazoles can be explained on the basis of molecular adsorption. The compounds inhibit corrosion by blocking both anodic and cathodic sites. In the present study the tested inhibitors have similar structure except for the substituents in the phenyl ring at position 2. In acidic solutions the benzothiazoles exist as protonated species. According to Prabhu et al [16] the protonated and

unprotonated species will exists in dynamic equilibrium. Electron donation by the unprotonated species to the anodic part of the metal surface through lone pair electrons over hetero atoms and π electrons of aromatic rings and back donation of electrons from the cathodic sites of the metal surface through protonated nitrogen of thiazole ring occur simultaneously [**Figure 12**]. In addition the phenyl ring in flat orientation may be involved in the electrostatic interaction through its delocalised π- electron with the metal atoms on the surface. TPB having three electron donating −OCH₃ groups in the phenyl ring has greater electron density on the phenyl ring, may be adsorbed more effectively than MPB and PBT and shows higher inhibition efficiency.
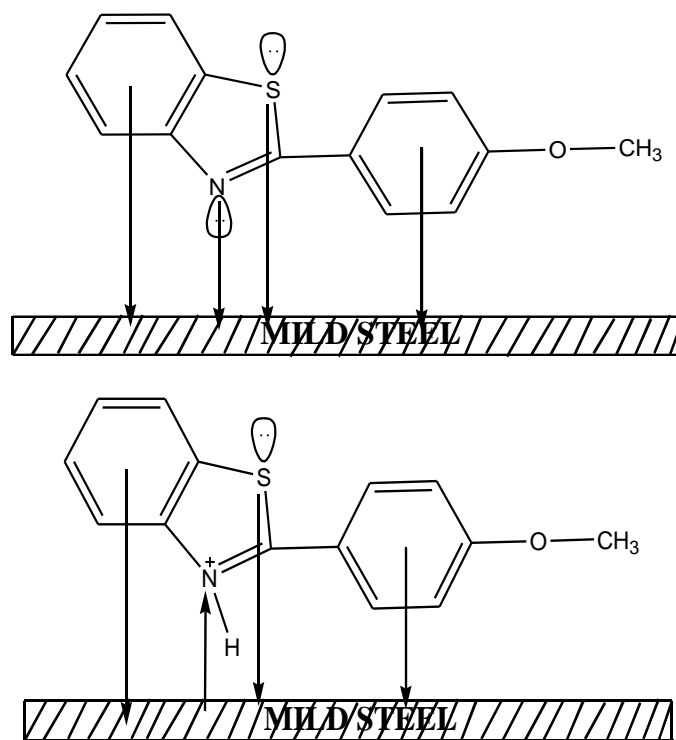

Figure 12 Adsorption of MPB and protonated MPB molecules on mild steel surface

Conclusion

The synthesised benzothiazoles have been proved to be promising inhibitors for mild steel corrosion in 1M sulphuric acid. They function by adsorption on the metal surface obeying Langmuir and Flory-Huggins adsorption isotherm and El-awady kinetic thermodynamic model. Polarization measurements revealed the benzothiazoles to be mixed type. SEM analysis confirms the corrosion of mild steel and its inhibition by the inhibitors.

Acknowledgement

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