

# Piperidine and Bispiperidine as Corrosion Inhibitor on Mild Steel in 1N Hydrochloric Acid Medium

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**Abstract**— In the present investigation of piperidine and bispiperidine have been synthesized and its inhibition action on the corrosion of mild steel in 1M HCl was studied by weight loss method, potentiodynamic polarization, electrochemical impedance, Atomic absorption spectroscopy (AAS), FTIR spectra, UV-adsorption spectroscopy. The inhibition efficiency increased with increase in inhibitor concentration. Temperature study was carried out and thermodynamic parameters such as change in enthalpy ( $\Delta H$ ), change in entropy ( $\Delta S$ ) and change in free energy ( $\Delta G$ ) were calculated. The results show that these compounds suppressed both anodic and cathodic process by adsorption on the surface which followed a Langmuir adsorption isotherm. Polarization measurements clearly indicate that all the examined compounds act as mixed inhibitors. Solution analysis by AAS for mild steel metal showed decreased dissolution of iron in the presence of inhibitors. FTIR-spectra confirmed the formation of the compounds. The surface morphology of the metals in presence and absence of the inhibitor was studied by using SEM images.

**Keywords:** Mild steel, corrosion, inhibition, adsorption and free energy.

## 1 INTRODUCTION

Annually greater than 85% of Mild Steel is produced because of their wide range of application in engineering material. The corrosion resistance of Mild Steel in various environments is due to the formation of thin and highly protective barrier oxide film that is bonded strongly to its surface. Therefore it is used in huge number of marine applications, chemical processing, refining of petroleum production, construction and metal-processing equipment [1]. Hydrochloric acid is widely used for the removal of rust and scale using several industrial operations. The presence of chloride may causes pitting corrosion on the steel alloys. The corrosion of carbon steel in such environments and its inhibition constitute a complex problem. In general, the hetero atoms [such as O, N or S, and multiple bonds] in organic compounds have shown good inhibiting properties to protect the metals against corrosion in acidic media [2-3]. However the use of these chemicals has been found to be expensive, toxic, nonbio-degradable and harmful to living things. Most corrosion inhibitors protect the corrosion of metals when they are adsorbed on the surface of the metal [4]. The most organic inhibitors get adsorbed on the metal surface by displacing water molecules and form a compact barrier film [5]. The availability of lone pairs and  $\pi$  electrons in the inhibitor molecules facilitates the electron transfer from the inhibitor to the metal, forming a coordinate covalent bond [6]. The strength of the adsorption bond depends on the electron density, on the donor atom of the functional group and also on the polarisability of the group [7].

In the present work an attempt has been made to synthesize few derivatives of piperidine and bispiperidine compounds and their anticorrosive property towards Mild steel in 1M HCl were evaluated using electrochemical and non-electrochemical methods. The chemical structure of the synthesized compounds was characterized by FTIR-Spectroscopy. The surface morphology of the metals characterized by SEM Analysis.

## 2.EXPERIMENTAL

### Weight loss Method

#### Specimen Preparation:

Mild Steel specimens of 3 x 1 x 0.5 were polished using 4/0, 3/0, 2/0 of emery sheets degreased with acetone and immediately used for experiments.

The initial weights of the polished plates were taken. A Blank Solution of the 1M HCl and the various concentration solutions of the Inhibitors were taken in a 100ml beaker and the metal specimens were suspended in the solution using glass hooks. Care was taken to ensure that the specimens were immersed completely in the solution and the specimen does not touch the walls of the beaker. After a period of one hour, the specimen were taken out, washed with running water, dried and weighed. From the initial and final weight of the specimen the weight loss was calculated. From the weight Loss data the inhibition efficiency, corrosion rate and the surface coverage were calculated using the following formulas.

$$\text{Corrosion rate} = \frac{534 \times W}{\text{DAT}} \quad (1)$$

Where, mpy = milli per year, W = Mass loss (mg), D = Density (gm/cm<sup>3</sup>), A = Area of specimen (cm<sup>2</sup>), T = time in hours.

$$\%IE = \frac{W_1 - W_2}{W_1} \times 100 \quad (2)$$

$$\Theta = \frac{W_1 - W_2}{W_1} \quad (3)$$

Where, W1 and W2 are the corrosion rates in the absence and presence of the inhibitor respectively.

From these values of (θ), a graph was drawn between C/θ Vs C or θ Vs Log C to obtain the best adsorption isotherm.

#### Temperature Studies:

The same procedure was carried out at different temperatures (303, 313, 323, and 333K) using a thermo stat to study the inhibition efficiency of the inhibitors at higher temperatures. This study gives details about the nature of the adsorption and activation energy.

The activation energy (Ea) was calculated by graphical method by plotting log (corrosion rate) Vs 1000/T (K) for higher Temperatures of 303, 313, 323, and 333 in 1M HCl with out and with inhibitor at all the concentration of inhibitors. Activation energy (Ea) was calculated for the inhibitor using the formula

$$E_a = -2.303 \times 8.314 \times \text{Slope (J)} \quad (4)$$

The free energy of adsorption ΔG ads has been calculated from the equilibrium constant of adsorption using the equation

$$\Delta G = -RT \times 2.303 \times \log (55.5K) \quad (5)$$

Where

$$K = \frac{\theta}{C(1-\theta)} \quad (6)$$

Θ = Surface coverage of the inhibitor

C = Concentration of the inhibitor in mM/100ml

K = equilibrium constant

R = gas constant

T = Temperature.

#### Electro chemical studies:

The electrochemical measurements were carried out in a glass cell with the capacity of 100ml. a platinum electrode and saturated calomel electrode used as a counter electrode and reference electrode respectively. The mild steel rod of size 0.6mm was taken and then placed in the test solution (uninhibited and inhibited solution) for 10- 15 minutes before electrochemical measurements.

The electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in a electrochemical

measurements unit. The EIS measurement was made at corrosion potential over a frequency range of 1MHz to 10MHz with signal amplitude of 10mV.

The Tafel polarization were made after EIS for a potential range of -200mV to + 200 mV with respect to open circuit potential, at a scan rate of 1mV/sec.

From Nysquist plot (Z real Vs Z imaginary) electrochemical resistance (Rt) and double layer capacitance Cdl were calculated.

From the plot of potential, E Vs log I, the corrosion potential Ecorr, corrosion current, Icorr and Tafels slope for the cathodic and anodic reaction bc and ba were obtained.

#### Inhibitor efficiency by potentiodynamic polarization method:

The inhibitor efficiency was calculated from the value of Icorr by using the formula

$$\text{Inhibition Efficiency (\%)} = \frac{I_{\text{corr (blank)}} - I_{\text{corr (inh)}}}{I_{\text{corr (blank)}}} \times 100 \quad (7)$$

Where,

Icorr (blank) = the corrosion current in the absence of the inhibitor. Icorr (inh) = the corrosion current in the presence of the inhibitor.

#### Inhibitor efficiency by AC impedance method:

The inhibitor efficiency was calculated using the formula

$$\text{Inhibition Efficiency (\%)} = \frac{R_t(\text{inh}) - R_t(\text{blank})}{R_t(\text{inh})} \times 100 \quad (7)$$

Where,

Rt (inh) = the charge transfer resistance in the presence of the inhibitor. Rt (blank) = the charge transfer resistance in the absence of the inhibitor.

#### IR spectra:

The IR spectra of the organic inhibitors are synthesized were recorded on a FT-IR spectrophotometer in the range 4000 – 400 cm<sup>-1</sup> using KBr disc technique. From the stretching and bending frequencies, information recording the various possible groups in the synthesized compounds was characterized.

### 3. RESULTS AND DISCUSSION

#### Weight loss method:

Weight loss, percentage of inhibition efficiency, corrosion rate and surface coverage for different concentrations (0.01, 0.03, 005 mM) of the inhibitors in 1M HCl are given in table (1).

From the table, it can be seen that the inhibition efficiency of inhibitor increases with increasing concentration of inhibitors for the mild steel. The maximum inhibition efficiency was obtained for mild steel at the inhibitor.

The variations in the weight loss with concentration are depicted graphically in the figure (1), it is clean that the weight loss decreases with increase in the inhibitor concentration, suggesting an increase in the number of molecules adsorbed

on the metal (mild steel) surface blocking the active sites of acid attack thereby protecting the metal from corrosion.

The variations in the inhibition efficiency with concentration are plotted graphically in the figure (2), inhibition efficiency increases with increase in the inhibitor concentration, suggesting inhibition depends upon the nature and mode of the adsorption of inhibitor on the metal surface.

The variation in the corrosion rate with concentration is shown in the figure (3), corrosion rate decreases with increase in inhibitor concentration. This is due to the presence of heteroatom's like nitrogen and aromatic ring.

Mild steel - DMP > BMDP

The best performance of DMP may be attributed to the presence of aromatic ring. The electron rich centre of the heteroatoms of the inhibitor molecules are potential centers of Lewis acid-base interaction with the metal surface. Although, the N-atoms in piperidine and bis piperidine have lone pair of electron, Lewis acid-base of the inhibitor with metal surface is more likely through the N-atoms [8].

#### Effect of temperature and thermodynamic parameters:

The effect of temperature on the corrosion behavior of mild steel was studied using weight loss measurements. The results obtained are shown in the tables (2) reveals that there is a progressive decrease in the inhibition efficiency as the temperature increases from 303-333 K.

Also an increase in temperature increases the solubility of the protective films on the metals thus increasing the susceptibility of the metals to corrosion [9].

Arrhenius plots for the corrosion rates of Mild steel with and without inhibitor for all the concentrations are given in figure (4, 5 & 6). The  $E_a$  values calculated are presented in the table (3). It has been proposed [10] that the higher  $E_a$  values imply a slow reaction and that the reaction is very sensitive to temperature. The increase in the activation energy in the presence of inhibitors signifies physical adsorption have low activation energy of the process in the presence of inhibitor compared to its absence is attributed to chemisorptions.

The  $E_a$  value for Mild steel in absence of the inhibitor in 1M HCl is 52.41KJ.

The values in the presence of the inhibitor were found to increase indicating the physical adsorption (or) weak bonding between the molecules of the inhibitor and the metal surface.

The increase of temperature enhances the rate of  $H^+$  ion diffusion to the metal surface beside the ionic mobility, which increases the conductivity of the electrolyte [11]. The increase in activation energy indicates that adsorption of the inhibitor molecule on the metal surface forms an energy barrier.

The experimental corrosion rate values obtained from the weight loss measurements in 1M HCl in the presence and absence of inhibitors was used to calculate the change in en-

thalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of activation for the formation of activation using the transition state equation.

A plot of  $\log (\text{Corrosion rate}/T)$  Vs  $1000/T$  gave a straight line with a slope of  $(-\Delta H^\circ / 2.303R)$  and an intercept of  $[\log(R/Nh) + \Delta S^\circ / 2.303R]$  from which the values of  $\Delta S^\circ$  and  $\Delta H^\circ$  were calculated and listed in the table(3).  $\Delta H^\circ$  are low confirming that the inhibitors were physically adsorbed.  $\Delta H^\circ$  was negative because inhibitor molecules are adsorbed onto the surface of the metals, and it is an exothermic reaction.  $\Delta S^\circ$  values increased in the presence of inhibitors compared to absence of inhibitors that freely moving in the bulk solution were adsorbed in an orderly fashion, this implies that the activated complex is the rate determining step represents association rather than dissociation, meaning that decrease in disordering takes place on going from reactant to the activated complex.

#### Adsorption isotherm

Adsorption of the inhibitor molecules mainly dependent on the charge and nature of the metal surface, electronic characteristics of the metal surface, temperature, adsorption of the solvent, ionic species and the electrochemical potential at the solution interface. The adsorption isotherm describes the adsorption behavior of organic compounds in order to know the adsorption mechanism. The most frequently used adsorption isotherms are Langmuir, Tempkin, Frumkin and Freundlich. To obtain the adsorption isotherm, the degree of surface coverage ( $\Theta$ ) was calculated for various concentrations of inhibitors from the weight loss data and listed in Table (1).

Adsorption behavior of piperidine and bis piperidine is best explained by Langmuir adsorption isotherm rather than other isotherms such as Tempkin, Frumkin and Freundlich. Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and adsorbent. Assumption of Langmuir relates the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage ( $\Theta$ ) according to the equation:

$$C/\Theta = 1/K + C \quad (8)$$

Where 'K' is the equilibrium constant of adsorption.

A liner plot behavior has been obtained when the graph is plotted between  $C/\Theta$  and C (fig 10). The  $R^2$  values obtained from the plots are very close to unity. This is because the interaction between the adsorbed species on the metal surface and those between the adsorbed organic molecules on the anodic and cathodic sites of the metal play important role in this process. This view is supported by Yadav[12] suggested that the inhibitor cover both anodic as well as the cathodic regions through general adsorption following Langmuir isotherm. Applicability of Langmuir adsorption isotherm to the adsorption of piperidine derivatives on mild steel confirms the formation of multimolecular layer of adsorption where there is

no interaction between the adsorbate and the adsorbent.

Free energy of the adsorption ( $\Delta G_{\text{ads}}^0$ ) calculated using

$$\Delta G_{\text{ads}}^0 = -RT \ln (55.5K) \quad (9)$$

Generally, values of  $\Delta G_{\text{ads}}^0$  upto  $-20\text{kJmol}^{-1}$  are consistent with electrostatic interaction between the charged molecules and the metal (physisorption) while those around  $-40\text{kJmol}^{-1}$  (or) higher are associated with chemisorptions. The values is lesser than  $-40\text{kJmol}^{-1}$  as shown in the table (4) indicating that all are physically adsorbed on the metal surface. The negative values of  $\Delta G_{\text{ads}}^0$  indicate the spontaneous adsorption of inhibitor on the surface of the metal[13] the absorption may be enhanced by the presence of nitrogen atoms with lone pair of electrons and the delocalized  $\pi$  electrons in the inhibitor molecules that makes it adsorbed electrostatically on the metal surface thus decreasing metal dissolution.

#### Electrochemical method:

#### Polarization studies

Potentiodynamic polarisation studies on the mild steel have been made for the inhibitors in 1M HCl. Typical polarization curves are presented in Fig(11). Corrosion kinetic parameters  $E_{\text{corr}}$ ,  $I_{\text{corr}}$ , Tafel (ba, bc) and inhibition efficiency are depicted in Table (5). The lower current density ( $I_{\text{corr}}$ ) values in the presence of inhibitors without causing significant changes in corrosion potential ( $E_{\text{corr}}$ ) suggest that the compounds are mixed type inhibitors and are adsorbed on the surface there by blocking the corrosion reaction. The Tafel constant ba and bc are both affected and there is no definite trend in the shift of  $E_{\text{corr}}$  values. This suggests that the compounds are mixed type inhibitors.

#### Electrochemical Impedance spectroscopy

Typical Nyquist plots obtained in the absence and presence of different concentrations of the inhibitors are shown in Fig (12). They are perfect semicircle and this may be attributed to the charge transfer reaction. The impedance parameters derived from Nyquist plots are presented in Table (6). From the table it is evident that as the concentration of the inhibitor increases,  $C_{dl}$  values decreases and  $R_t$  values increases. Decrease of  $C_{dl}$  is due to an increase in the thickness of the electrical double layer. This suggests that the inhibitor molecules function by adsorption at the metal solution interface.

#### Atomic absorption spectral measurements

Atomic absorption spectroscopic method measures the concentration of ions in the solution. The dissolution of iron was measured by calculating the dissolved iron in the corrode solution with and without inhibitor. The results are presented in the tables (7). The percentage inhibition efficiency obtained by this technique was found to be in good agreement with that obtained from the conventional method.

#### Surface morphology (SEM)

The surface morphology of as-corroded uninhibited and inhibited Mild steel in 1M HCl after 2-hours of immer-

sion were examined with scanning electron microscopy. Figure (14, 15) shows photograph of the plate with and without inhibitor in hydrochloric acid media. The sample without inhibitor showed pits, but in presence of inhibitor the pits was minimized on the metal surface. It indicates the formation of passive layer on the metal surface. So the corrosion rate is decreased in the presence of inhibitor and reduces the electrochemical reaction.

#### FTIR- spectroscopy

The synthesized inhibitor was confirmed by the IR data. The figures (13) showed the formation of the compound.

Stage 1: DMP: C=O -1697.43, N-H - 1647.28, M-substituted benzene - 795.73.

Stage 2 : BMDP: N-N - 1540, C-OH - 1355.05, M-substitutedbenzene - 820.71

In the stage 1 we found a peak near 1697.43 for C=O but in stage 2 we only found the peak near 1540 this confirms the structure of the synthesized inhibitors.

#### CONCLUSION:

1. Traditional weight loss revealed that all the synthesized compounds act as a good inhibitor for Mild steel.
2. The activation energy of the corrosion process increases in presence of all the inhibitors in mild steel indicating physical adsorption.
3. The change in free energy carries negative values which indicate that the adsorption process is spontaneous and physically adsorbed.
4. Enthalpy of activation values obtained for the inhibitors (DMP, BHMP, BMDP, BHMPH) in Mild steel is negative indicates endothermic process.
5. Entropy of activation obtained are in positive indicating the system disorder for the inhibitors (DMP, BHMP) in the mild steel metal.
6. Adsorption of the four inhibitors in the Mild steel metal at 303 K is found to follow the Langmuir adsorption isotherm.
7. Electrochemical techniques revealed that all the inhibitors for the Mild steel metal are of mixed type.
8. Atomic adsorption spectroscopy (AAS) the observed result was in good agreement with the conventional method with Mild steel for the two inhibitors (DMP, BHMP).

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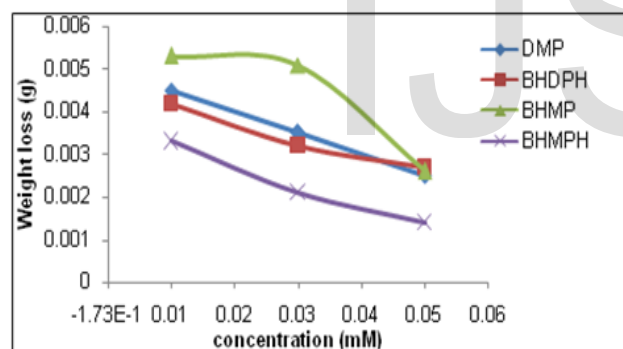


Figure 1 : Effect of concentration on the weight loss of inhibitors for Mild steel in 1M HCl

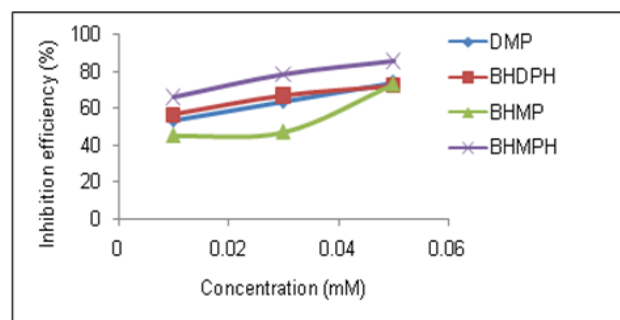


Figure 2: Effect of Concentration on the Inhibition efficiency of inhibitors for Mild steel in 1M HCl

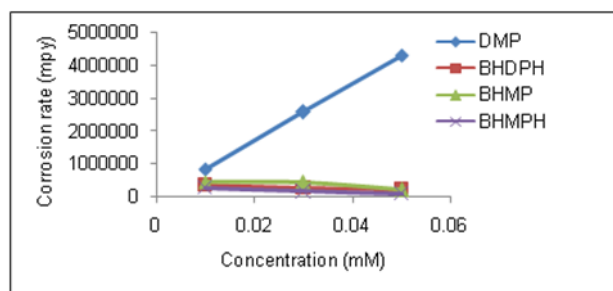


Figure 3: Effect of Concentration on the Corrosion rate of inhibitors for mild steel in 1M HCl

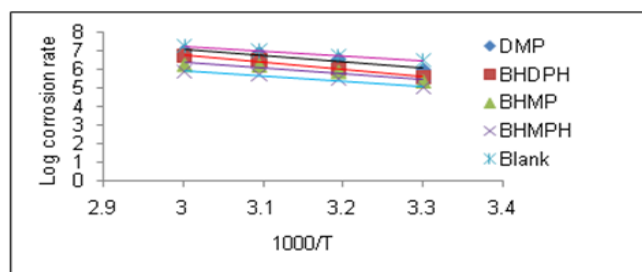


Figure 4: Arrhenius plot of corrosion of Mild steel in 1M HCl solution in the absence and presence of 0.01 mM concentration of the Inhibitors

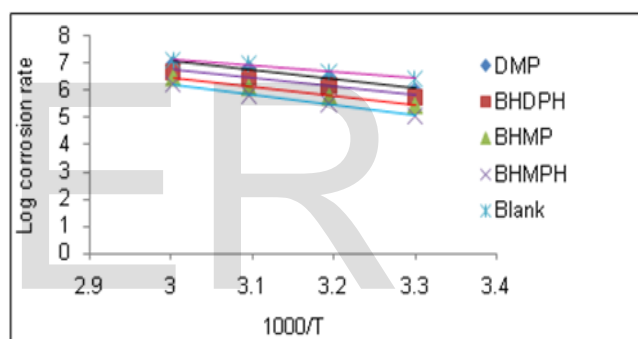


Figure 5: Arrhenius plot of corrosion of Mild steel in 1M HCl solution in the absence and presence of 0.03 mM concentration of the Inhibitors

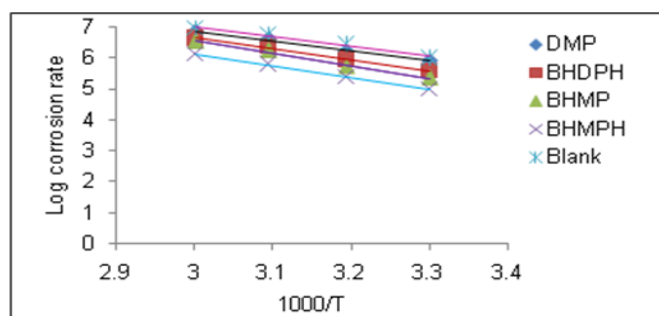


Figure 6: Arrhenius plot of corrosion of Mild steel in 1M HCl solution in the absence and presence of 0.05 mM concentration of the Inhibitors

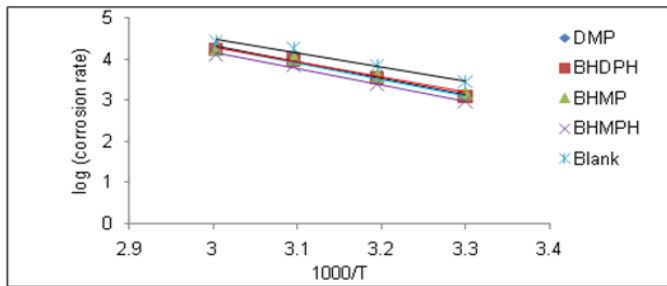


Figure 7: Transition plot of corrosion of Mild steel in 1M HCl solution in the absence and presence of 0.01 mM concentration of the Inhibitors

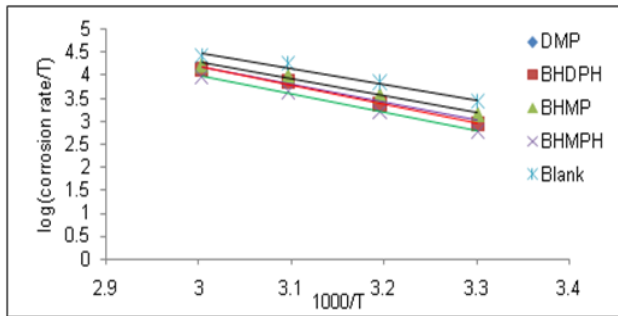


Figure 8: Transition plot of corrosion of Mild steel in 1M HCl solution in the absence and presence of 0.03 mM concentration of the Inhibitors

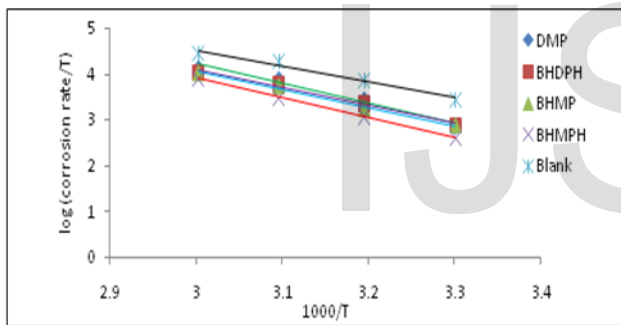


Figure 9: Transition plot of corrosion of Mild steel in 1M HCl solution in the absence and presence of 0.05 mM concentration of the Inhibitors

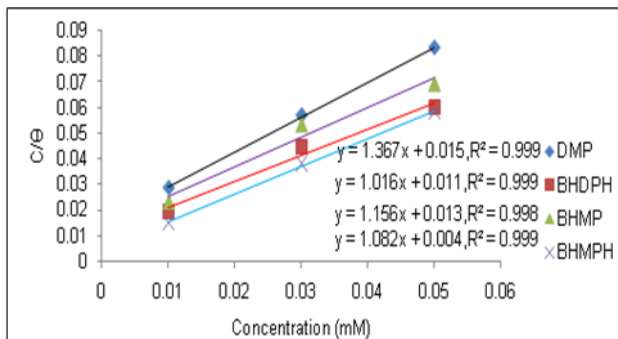


Figure 10: Langmuir plot for Mild steel of inhibitors in 1M HCl at Room temperature

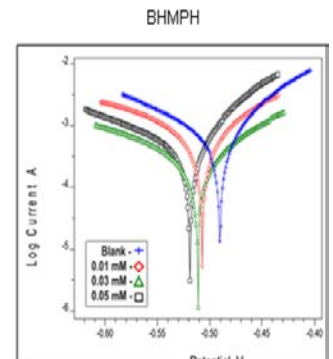
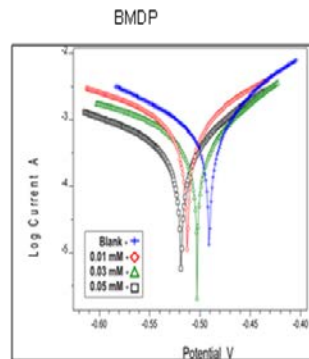
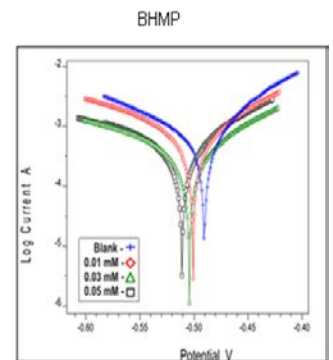
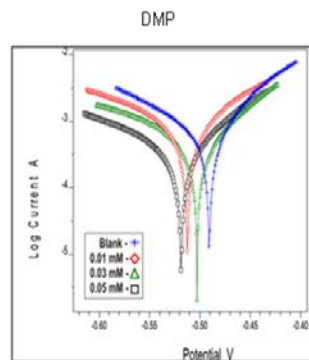


Figure 11 Polarization curves the inhibitors

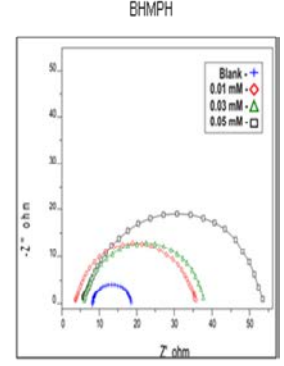
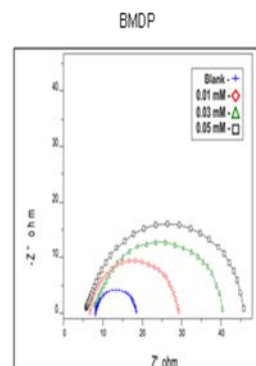
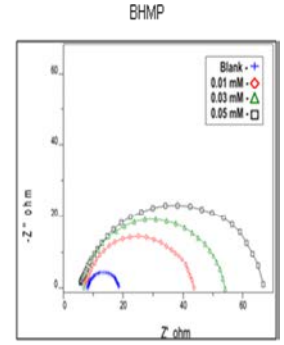
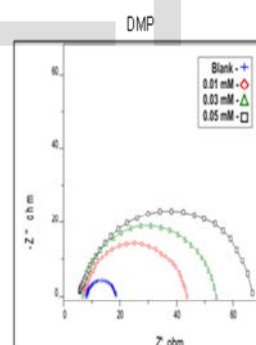


Figure 12  
Nyquist diagram for Mild steel in 1M HCl

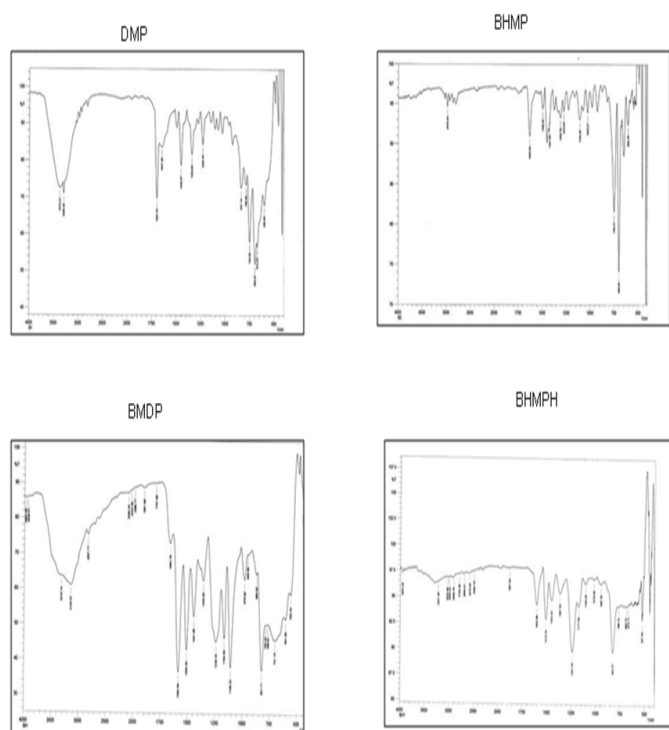


Figure 13: IR Data for the Inhibitors

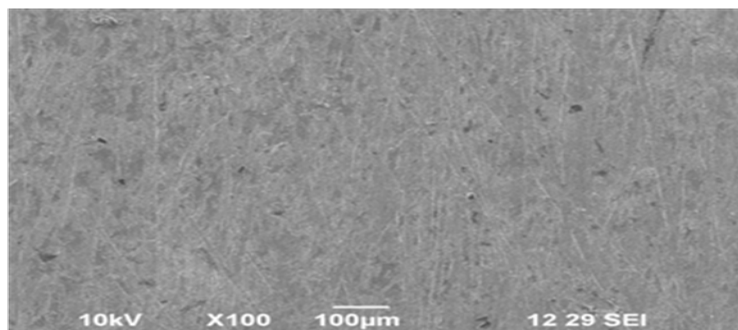


Figure 14: SEM photograph for mild steel dipped in 1 M HCl

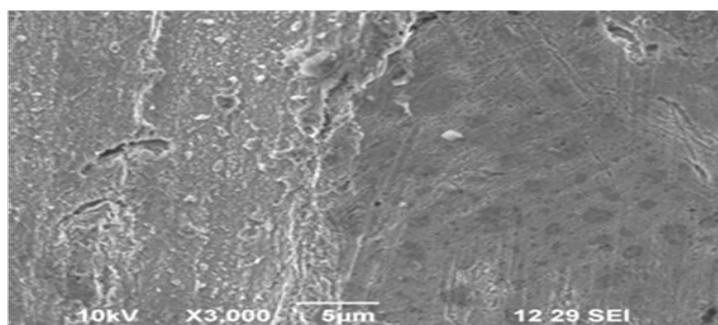


Figure 15: SEM photograph for mild steel dipped in 1 M HCl containing DMP

TABLE 1

Inhibition efficiencies of mild steel in various concentration of inhibitor (DMP, BHMP, BMDP, BHMPH) in 1M HCl by weight loss measurement at room temperature

Name of the Inhibitor	Inhibitor Concentration (mM)	Weight loss (g)	Inhibition Efficiency (%)	Corrosion Rate (mpy)	Degree of surface Coverage (θ)
DMP	Blank	0.0097	-	834287.5	-
	0.01	0.0045	53.60	387040.6	0.536
	0.03	0.0035	63.91	301031.6	0.6391
	0.05	0.0025	74.22	215022.5	0.7422
BHMP	Blank	0.0097	-	834287.5	-
	0.01	0.0042	56.70	361237.9	0.567
	0.03	0.0032	67.01	275228.9	0.6701
	0.05	0.0027	72.16	232224.3	0.7216
BMDP	Blank	0.0097	-	834287.5	-
	0.01	0.0053	45.36	455847.8	0.4536
	0.03	0.0051	47.42	438646	0.4742

	0.05	0.0026	73.19	223623.4	0.7319
BHMPH	Blank	0.0097	-	834287.5	-
	0.01	0.0033	65.97	283829.8	0.6597
	0.03	0.0021	78.35	180618.9	0.7835
	0.05	0.0014	85.56	120412.6	0.8556

Table 2

Inhibition efficiencies of various concentration of inhibitor (DMP, BHMP, BMDP, BHMPH) in 1M HCl by weight loss measurement at higher temperature

Name of the Inhibitor	Temperature (K)	Inhibitor Concentration (mM)	Weight loss (g)	Inhibition Efficiency (%)	Corrosion Rate (mpy)	Degree of surface Coverage(θ)
DMP	303	Blank	0.0097	-	834287.5	-
		0.01	0.0045	53.60	387040.6	0.5360
		0.03	0.0035	63.91	301031.6	0.6391
		0.05	0.0025	72.22	232224.3	0.7222
	313	Blank	0.0255	-	2193230	-
		0.01	0.0128	49.80	1100915	0.4980
		0.03	0.0107	58.03	920296.5	0.5803
		0.05	0.0100	60.78	860090.2	0.6078
	323	Blank	0.0678	-	5831411	-
		0.01	0.042	38.05	3612379	0.3805
		0.03	0.0292	56.93	2511463	0.5693
		0.05	0.0286	57.81	2459853	0.5781
	333	Blank	0.1022	-	870121	-
		0.01	0.0729	28.66	6270057	2866
		0.03	0.0549	46.28	4721895	4628
		0.05	0.0508	50.29	4369258	5029s
BHMP	303	Blank	0.0097	-	834287.5	-
		0.01	0.0042	56.70	361237.9	0.5670
		0.03	0.0032	67.01	275228.9	0.6701
		0.05	0.0025	74.22	215022.5	0.7422
	313	Blank	0.0255		2193230	



		0.01	0.0124	51.37	1066512	0.5137
		0.03	0.0088	65.49	756879	0.6549
		0.05	0.0081	68.23	696673	0.6823
	323	Blank	0.0678	-	5831411	-
		0.01	0.0357	47.34	3070522	0.4734
		0.03	0.0286	57.81	2459858	0.5781
		0.05	0.0217	67.99	1866396	0.6799
	333	Blank	0.1022	-	8790121	-
		0.01	0.0645	36.88	5547582	0.3688
		0.03	0.0542	46.96	4661689	0.4696
		0.05	0.0405	60.37	3483365	0.6037
BMDP	303	Blank	0.0097	-	834287.5	-
		0.01	0.0053	45.36	45587.8	0.4536
		0.03	0.0051	47.42	438646	0.4742
		0.05	0.0026	73.19	223623.4	0.7319
	313	Blank	0.0255	-	2193230	-
		0.01	0.0141	44.70	1212727	0.4470
		0.03	0.0137	46.27	1178324	0.4627
		0.05	0.0061	72.54	524655	0.7254
	323	Blank	0.0678	-	5831411	-
		0.01	0.0394	41.88	3388755	0.4188
		0.03	0.0368	45.72	3165132	0.4572
		0.05	0.02	70.50	1720180	0.7050
	333	Blank	0.1022	-	8790121	-
		0.01	0.0689	32.52	5926021	0.3252
		0.03	0.0658	35.61	5659393	0.3561
		0.05	0.0402	60.60	3457562	0.6060
BHMPH	303	Blank	0.0097	-	834287.5	-
		0.01	0.0033	65.97	283829.8	0.6597
		0.03	0.0021	78.35	180618.9	0.7835
		0.05	0.0014	85.56	120412.6	0.8556

	313	Blank	0.0255	-	2193230	-
		0.01	0.0091	64.31	782682	0.6431
		0.03	0.0058	77.25	498852.3	0.7725
		0.05	0.0043	83.13	369838.8	0.8313
	323	Blank	0.0678	-	5831411	-
		0.01	0.0264	61.50	2270638	0.6150
		0.03	0.017	74.12	1462153	0.7412
		0.05	0.0114	82.44	980502.8	0.8244
	333	Blank	0.1022	-	8790121	-
		0.01	0.0502	50.88	4317653	0.5088
		0.03	0.0359	64.87	3087724	0.6487
		0.05	0.0299	70.74	2571670	0.7074

Table 3  
Thermodynamic parameters for mild steel in 1M HCl at different concentration of corrosion Inhibitor

Inhibitor Concentration (mM)	Name of the Inhibitor	$-\Delta H^\circ$ KJ/mole	$\Delta S^\circ$ KJ/mole/K
0.01	Blank	12.27	53.92
	DMP	14.63	60.48
	BHMP	14.17	58.88
	BMDPH	13.33	56.43
	BHMPH	14.13	58.31
0.03	Blank	12.27	53.92
	DMP	14.19	58.66
	BHMP	14.82	60.51
	BMDPH	13.23	56.04
	BHMPH	14.69	59.41
0.05	Blank	12.27	53.92
	DMP	15.52	62.66
	BHMP	13.95	57.45
	BMDPH	14.38	58.64
	BHMPH	15.57	61.70

Table 4  
Activation energy ( $E_a$ ) and free energy ( $\Delta G^\circ_{ads}$ ) for Mild steel the corrosion in 1M HCl at 0.01, 0.03, 0.05 mM concentration of the inhibitors

Inhibitor Concentration(mM)	Name of the inhibitor	Activation energy ( $E_a$ ) KJ	Gibb's Free energy( $\Delta G^\circ_{ads}$ ) at various temperature			
			303	313	323	333
0.01	Blank	52.41	-	-	-	-
	DMP	65.08	-9.59	-9.73	-9.48	-9.26
	BHMP	77.83	-9.72	-9.80	-9.93	-9.72

	BMDPH	60.20	-9.22	-9.50	-9.67	-9.48
	BHMPH	54.12	-10.15	-10.40	-10.60	-10.40
0.03	Blank	52.41	-	-	-	-
	DMP	64.52	-8.85	-8.86	-9.09	-8.86
	BHMP	60.14	-9.00	-9.22	-9.914	-8.89
	BMDPH	64.86	-8.11	-8.33	-8.57	-8.34
	BHMPH	71.61	-9.63	-9.88	-10.00	-9.78
0.05	Blank	52.41	-	-	-	-
	DMP	59.50	-8.82	-8.41	-8.54	-8.44
	BHMP	70.72	-8.71	-8.78	-9.05	-8.93
	BMDPH	72.50	-8.77	-9.02	-9.19	-8.94
	BHMPH	78.9`	-9.61	-9.72	-9.98	-9.49

Table 5  
Potentiodynamic polarization parameters for the corrosion of Mild steel in  
1 M HCl with and without inhibitor

Name of the inhibitor	Inhibitor concentration (mM)	$I_{corr}(\mu A/cm^2) \times 10^2$	$E_{corr}$ (mV vs SCE)	$\beta_c$ (mV/dec)	$\beta_a$ (mV/dec)	Inhibition efficiency (%)
DMP	Blank	111	-0.4106	0.113	0.069	-
	0.01	23.5	-0.2016	0.112	0.066	50.72
	0.03	54.7	-0.208	0.138	0.071	62.07
	0.05	42.1	-0.2164	0.148	0.070	78.82
BHMP	Blank	111	-0.4106	0.113	0.069	-
	0.01	70.3	-0.1624	0.141	0.082	36.66
	0.03	59.2	-0.1653	0.146	0.070	46.66
	0.05	45.8	-0.1666	0.138	0.075	58.78
BMDPH	Blank	111	-0.4106	0.113	0.069	-
	0.01	51.1	-0.1735	0.126	0.075	50.36
	0.03	55.1	-0.1712	0.140	0.081	53.96
	0.05	48.0	-0.1796	0.143	0.080	56.76
BHMPH	Blank	111	-0.4106	0.113	0.069	-
	0.01	34.9	-0.1786	0.132	0.075	60.77
	0.03	11.5	-0.1718	0.134	0.084	68.55
	0.05	43.6	-0.2006	0.141	0.061	89.63

Table 6  
Impedence polarization parameters for the corrosion of Mild steel in  
1 M HCl with and without inhibitor

Name of the inhibitor	Inhibitor concentration (mM)	$R_{ct}$ (ohms)	$C_{dl}$ (farads $\times 10^5$ )	Inhibition efficiency (%)
DMP	Blank	0.71	6.50	-
	0.01	23.33	2.39	96.95
	0.03	33.41	3.37	97.87
	0.05	42.25	3.62	98.31
BHMP	0.01	14.43	3.50	95.07
	0.03	21.57	3.81	96.70
	0.05	29.97	3.91	97.63
BMDPH	0.01	12.64	4.57	94.38
	0.03	19.54	2.79	96.36
	0.05	28.72	4.75	97.52
BHMPH	0.01	24.48	6.62	97.09
	0.03	21.57	3.89	96.84
	0.05	35.24	3.82	98.26

Table 7  
Amount of dissolved Mild steel present in the corrosive solution (1M HCl)  
containing selected concentration by AAS

S.no	Name of the inhibitor	Inhibitor concentration (mM)	Amount of Mild steel in corrodant (mg/l)	Inhibition Efficiency (%)
1.	DMP	Blank	90.45	-
		0.03	36.31	59.85
2.	BHMP	Blank	90.45	-
		0.03	34.78	61.54