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## Adsorption and Corrosion-Inhibiting Effect of 5-Benzyloxy-6-methoxyindole on Mild Steel Surface in Hydrochloric Acid Solution: Electrochemical and Monte Carlo simulation studies.

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### ABSTRACT

The potential of 5-Benzyloxy-6-methoxyindole, noted BMI as a corrosion inhibitor of mild steel in 1 M HCl was determined using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods (*EIS*). Maximum inhibition was attained at the concentration of  $5 \cdot 10^{-3}$  M. The inhibition efficiencies of BMI obtained from the impedance and polarization measurements were in good agreement where the maximum inhibition is around 91%. Potentiodynamic polarization measurement studies revealed that BMI behave as mixed inhibitor. The adsorption of BMI was found to follow Langmuir's adsorption model. Molecular modeling by Monte Carlo simulation was used to evaluate the structural, electronic and reactivity parameters of the indole derivative in relation to their effectiveness as corrosion inhibitor.

**Keywords:** Corrosion inhibition, Mild steel, *EIS*, Weight loss, Monte Carlo simulation

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## INTRODUCTION

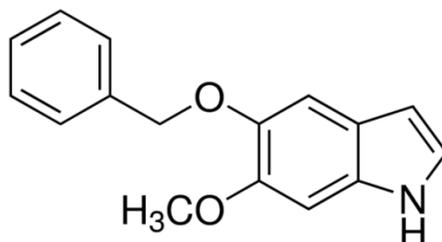
The use of inhibitors is one of the most practical methods for protection of metals against corrosion especially in acidic media. The use of corrosion inhibitors is considered as the most effective method for the protection of many metals and alloys against such acid attack[1–6]. Compounds containing functional groups with heteroatoms, which can donate one pair of electrons, are found to be very efficient as inhibitors against metal corrosion in many environments[7–14]. Many heterocyclic compounds with polar groups and/or  $\pi$  electrons are efficient corrosion inhibitors in acidic solutions. Organic molecules of this type can adsorb on the metal surface and form a bond between their N-electron pair and/or  $\pi$  electron cloud and the metal surface, thereby reducing the corrosion in acidic solutions[15–20]. In continuation of our studies, we report for the first time the use of 5-Benzyloxy-6-methoxyindole as acid corrosion inhibitor for mild steel surface in hydrochloric acid solution using gravimetric method, electrochemical measurements. Thermodynamic parameters, together with molecular dynamic simulation using Monte Carlo method were further employed to provide additional insight into the mechanism of inhibitory action.

## MATERIALS AND METHODS

### Electrodes, Gravimetric and Electrochemical measurements

Corrosion tests have been performed, using the gravimetric and electrochemical measurements, on electrodes cut from sheets of carbon steel with the chemical composition: 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu, and the remainder iron. The aggressive medium of molar hydrochloric acid used for all studies were prepared by dilution of analytical grade 37% HCl with double distilled water. The concentrations of BMI used in this investigates were varied from  $10^{-4}$  to  $5.10^{-3}$  M. The inhibitor molecule used in this paper was purchased from Sigma–Aldrich and have the structure presented in Fig. 1.

Figure 1. Chemical structure of tested compound.



Gravimetric measurements were realized in a double walled glass cell equipped with a thermostat-cooling condenser. The carbon steel specimens used have a rectangular form with dimension of  $2.5 \times 2.0 \times 0.2$  cm were abraded with a different grade of emery paper (320-800-1200) and then washed thoroughly with distilled water and acetone. After weighing accurately, the specimens were immersed in beakers which contained 100 ml acid solutions without and with various concentrations of BMI at temperature equal to 303 K remained by a water thermostat for 6h as immersion time. The gravimetric tests were performed by triplicate at same conditions.

The corrosion rates ( $C_R$ ) and the inhibition efficiency ( $\eta_{wt}$  %) of carbon steel have been evaluated from mass loss measurement using the following equations:

$$C_R = \frac{w}{St} \quad (1)$$

$$\eta_{wt} \% = \frac{C_R^0 - C_R}{C_R^0} \times 100 \quad (2)$$

Where  $w$  is the average weight loss before and after exposure, respectively,  $S$  is the surface area of sample,  $t$  is the exposure time,  $C_R^0$  and  $C_R$  is the corrosion rates of steel without and with the BMI inhibitor, respectively.

The potentiodynamic polarization curves were conducted using an electrochemical measurement system PGZ 100 Potentiostat/Galvanostat controlled by a PC supported by the Voltmaster 4.0 Software. The electrochemical measurements were performed in a conventional three electrode glass cell with carbon steel as a working electrode, platinum as counter electrode (Pt) and a saturated calomel electrode used as a reference electrode. The working electrode surface was prepared as described above gravimetric section. Prior to each electrochemical test an immersion time of 30 min was given to allow the stabilization system at corrosion potential. The polarization curves were obtained by changing the electrode potential automatically from -800 to -200 mV/SCE at a scan rate of 1 mV s<sup>-1</sup>. The temperature is thermostatically controlled at desired temperature ±1K. The percentage protection efficiency ( $\eta_p\%$ ) is defined as:

$$\eta_{PDP}(\%) = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100 \quad (3)$$

Where,  $I_{corr}^0$  are corrosion current in the absence of inhibitor,  $I_{corr}$  are corrosion current in the presence of inhibitor.

Electrochemical impedance spectroscopy (EIS) measurements were carried out with same equipment used for potentiodynamic polarization study (Voltalab PGZ 100) at applied sinusoidal potential waves of 5mV amplitudes with frequencies ranging from 100 KHz to 10 mHz at corrosion potential. The impedance diagrams are given in the Nyquist representation. The charge transfer resistance ( $R_{ct}$ ) was determined from Nyquist plots and double layer capacitance ( $C_{dl}$ ) was calculated from CPE parameters of the equivalent circuit deduced using Zview software. In this case the percentage protection efficiency ( $\eta_{EIS}\%$ ) is can be calculated by the value of the charge transfer resistance ( $R_{ct}$ )

$$\eta_{EIS}(\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (4)$$

Where  $R_{ct}^0$  and  $R_{ct}$  were the polarization resistance of uninhibited and inhibited solutions, respectively.

### Monte Carlo simulation study

The Monte Carlo (MC) search was adopted to compute the low configuration adsorption energy of the interactions of the BMI on a clean iron surface. The Monte Carlo (MC) simulation was carried out using Materials Studio 6.0 software (Accelrys, Inc.) [21]. The Fe crystal was cleaved along the (1 1 0) plane, it is the most stable surface as reported in the literature. Then, the Fe (1 1 0) plane was enlarged to (10x10) supercell to provide a large surface for the interaction of the inhibitor. The simulation of the interaction between BMI and the Fe (1 1 0) surface was carried out in a simulation box (24.82 × 24.82 × 30.13 Å) with periodic boundary conditions, which modeled a representative part of the interface devoid of any arbitrary boundary effects. After that, a vacuum slab with 30 Å thickness was built above the Fe (1 1 0) plane. All simulations were implemented with the COMPASS force field to optimize the structures of all components of the system of interest. More simulation details on the methodology of Monte Carlo simulations can be found in previous publications [22–24].

## RESULTS AND DISCUSSION

### Gravimetric measurements

Weight loss measurement is a non-electrochemical technique for the determination of corrosion rates and inhibitor efficiency, which provides more reliable results than electrochemical techniques because the experimental conditions are approached in a more realistic manner yet the immersions tests are time-consuming. Therefore, due to such differences (experimental conditions); the values would obviously differ from the electrochemical values [15,16]. Table 1 shows the percentage of inhibition efficiency ( $IE\%$ ) for BMI at the temperature of 303 K. From the table, it was revealed that as the concentrations of the inhibitor increased, the percentage of inhibition efficiency was also increased (concentration-dependent). The optimum value of inhibition was obtained at the concentration of  $5.10^{-3}$  M. This indicates that the adsorption process between the adsorbate (inhibitor) and the mild steel surface was efficiently achieved and led to the formation of a

strong metal–inhibitor interaction, thus lowering the capability of chloride ion ( $\text{Cl}^-$ ) to adsorb on the mild steel surface[17,18].

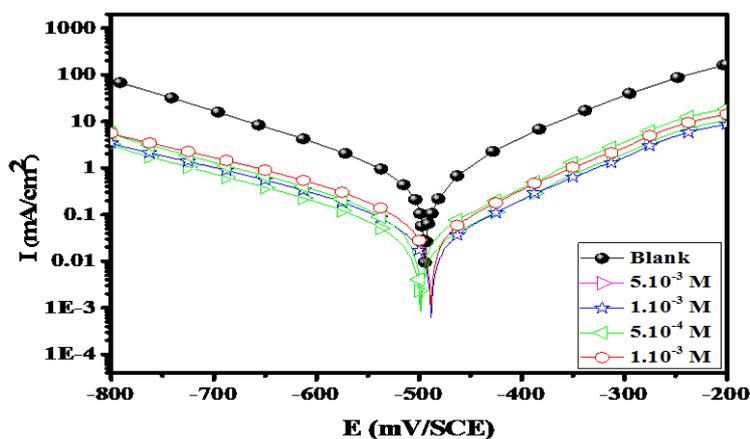
**Table 1: Inhibition efficiency of various concentrations of BMI for corrosion of MS in 1M HCl obtained by weight loss measurements at 303K.**

Inhibitors	Concentration (M)	$C_R$ ( $\text{mg cm}^{-2} \text{h}^{-1}$ )	$\eta_w$ (%)	$\Theta$
Blank	1.0	1.135	-	-
BMI	$5.10^{-3}$	0.0837	92.62	0.9262
	$1.10^{-3}$	0.1311	88.45	0.8845
	$5.10^{-4}$	0.1848	83.72	0.8372
	$1.10^{-4}$	0.2266	80.03	0.8003

### Polarization results

Fig. 2 show anodic and cathodic polarisation plots recorded on mild steel electrode in 1 M HCl in absence and presence of different concentrations of our inhibitor (BMI). Table 2 shows the electrochemical corrosion kinetic parameters, i.e., corrosion potential ( $E_{\text{corr}}$ ), cathodic Tafel slope ( $\beta_c$ ) and corrosion current density  $i_{\text{corr}}$  obtained by extrapolation of the Tafel lines. As it was expected, both anodic and cathodic reactions of mild steel electrode corrosion were inhibited by the increase of the indole derivative. This result suggests that the addition of the inhibitor reduces anodic dissolution and retards the hydrogen evolution reaction[25,26]. At a concentration of  $5.10^{-3}$  M BMI exhibits maximum inhibition efficiency (91.36%). It can be seen that the corrosion rate is decreased and inhibition efficiency  $IE$  (%) is increased by increasing inhibitor concentration. This inhibitor cause insignificant change in the cathodic Tafel slope and no definite trend was observed in the shift of  $E_{\text{corr}}$  values in the presence of different concentrations of the indole derivative, suggesting that this compound behave as mixed-type (anodic/cathodic) inhibitor[7,17]. Increase in inhibition efficiencies with the increase of concentrations of studied inhibitor shows that the inhibition actions are due to its adsorption on mild steel surface[19].

**Figure 2. Polarisation curves of MS in 1 M HCl for various concentrations of BMI at 303K.**



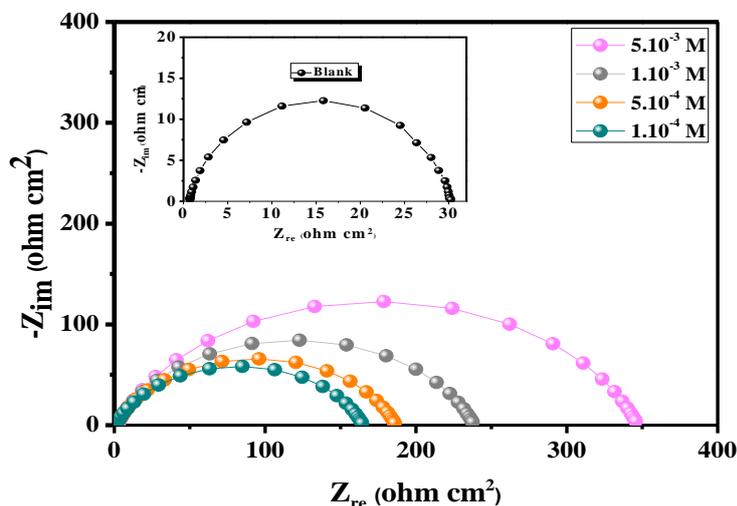
**Table 2. Corrosion parameters for corrosion of MS with selected concentrations of BMI in 1M HCl by Potentiodynamic polarization method at 303K.**

Inhibitor	Concentration (M)	$-E_{\text{corr}}$ (mV/SCE)	$-\beta_c$ ( $\text{mV dec}^{-1}$ )	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	$\eta_{\text{Tafel}}$ (%)	$\Theta$
Blank	-	496	162.0	564.0	-	-
BMI	$5.10^{-3}$	500	168.7	48.7	91.36	0.9136
	$1.10^{-3}$	493	174.1	65.2	88.44	0.8844
	$5.10^{-4}$	503	169.6	85.8	84.78	0.8478
	$1.10^{-4}$	491	173.2	106.2	81.17	0.8117

### Electrochemical Impedance Spectroscopy study

The corrosion behavior of mild steel in 1 M HCl solution in the presence of BMI was investigated by EIS at 303 K after 30 min of immersion. The Nyquist plots for mild steel obtained at the interface in the presence and absence of BMI at different concentrations are given in Figure 3.

Figure 3. Nyquist curves for mild steel in 1M HCl for selected concentrations of BMI at 303K.



As observed, the Nyquist plots contain a depressed semi-circle with the center below the real x-axis, which is size increased by increasing the inhibitor concentrations, indicating that the corrosion is mainly a charge transfer process and the formed inhibitive film was strengthened by the addition of the compound[20]. The depressed semi-circle is the characteristic of solid electrodes and often refers to the frequency dispersion which arises due to the roughness and other inhomogeneities of the surface[18]. It is worth noting that the change in concentration of BMI did not alter the style of the impedance curves, suggesting a similar mechanism of the inhibition is involved[15]. The impedance parameters derived from these plots are shown in Table 3. The impedance spectra were fitted to the Rs(RctCPE) equivalent circuit of the form in Fig. 4. Where  $R_s$  is the solution resistance,  $R_{ct}$  denotes the charge-transfer resistance and CPE is constant phase element. The introduction of CPE into the circuit was necessitated to explain the depression of the capacitance semicircle, which corresponds to surface heterogeneity resulting from surface roughness, impurities, and adsorption of inhibitors[18]. The impedance of this element is frequency-dependent and can be calculated using the Eq. 5[20]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \quad (5)$$

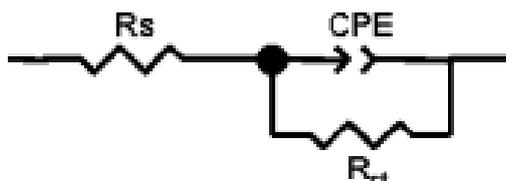
Where  $Q$  is the CPE constant (in  $\Omega^{-1} S^n cm^{-2}$ ),  $\omega$  is the angular frequency (in  $rad s^{-1}$ ),  $j^2 = -1$  is the imaginary number and  $n$  is a CPE exponent which can be used as a gauge for the heterogeneity or roughness of the surface[27]. In addition, the double layer capacitances,  $C_{dl}$ , for a circuit including a CPE were calculated by using the following Eq. 6:

$$C_{dl} = (Q \cdot R_{ct}^{1-n})^{1/n} \quad (6)$$

The decrease in the values of  $C_{dl}$  follows the order similar to that obtained for the  $i_{corr}$  studies. This can be explained on the basis of compound adsorption on the metal surface leading to the formation of a surface film in the acidic solution[15,19]. The impedance study also gave the same efficiency trend as found in Tafel polarisation methods.

**Table 3. AC-impedance parameters for corrosion of mild steel for selected concentrations of BMI in 1M HCl at 303K.**

Inhibitor	Concentration (M)	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$n$	$Q \times 10^{-4}$ ( $\text{s}^n \Omega^{-1} \text{cm}^{-2}$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	$\eta_{EIS}$ (%)	$\theta$
Blank	1.0	29.35	0.910	1.7610	91.6	-	-
BMI	$5.10^{-3}$	345	0.882	0.2887	15.58	91.49	0.9149
	$1.10^{-3}$	237.2	0.861	0.4776	23.17	87.62	0.8762
	$5.10^{-4}$	185.4	0.903	0.6223	38.53	84.16	0.8416
	$1.10^{-4}$	163.9	0.895	0.7078	41.96	82.09	0.8209

**Figure 4. Equivalent electrical circuit model**


### Adsorption isotherm

It is generally assumed that the adsorption of the inhibitors on the metal surface is the essential step in the inhibition mechanism and the adsorption isotherm is a convenient way to characterize the metal/inhibitor/environment system[13,19,20]. The establishment of isotherms that describe the adsorption behavior of inhibitor is important to research the nature of metal–inhibitor interaction. The degree of surface coverage ( $\theta$ ) at different concentration of investigated inhibitor on the corrosion of mild steel were calculated using the weight loss results. In 1 M HCl, BMI adsorption follows the Langmuir isotherm (Fig. 5) as per Eq.7[8]:

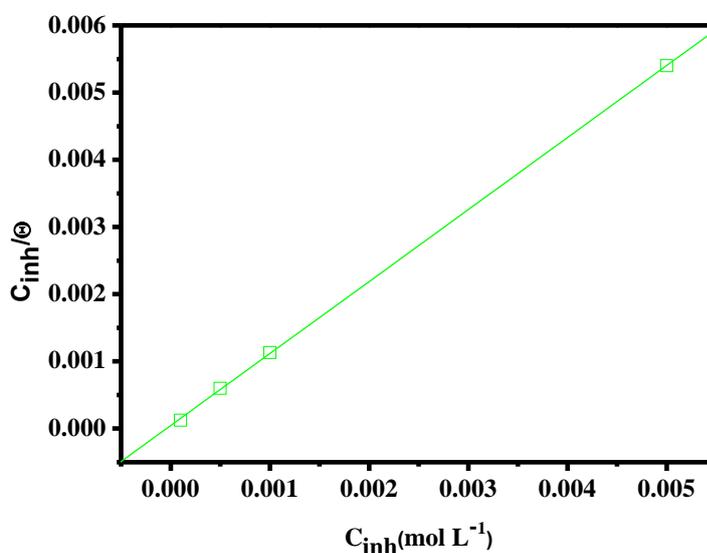
$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (7)$$

Where,  $C$  is the concentration of the inhibitor,  $K_{ads}$  is the equilibrium constant of adsorption and  $\theta$  is the surface coverage. The Langmuir approach is based on a molecular kinetic model of the adsorption–desorption process. On the other hand, the adsorption equilibrium constant ( $K_{ads}$ ) is related to the standard free energy of adsorption ( $\Delta G^{\circ}_{ads}$ ) of the inhibitor molecules by the following Eq. 8[26]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \quad (8)$$

Where  $R$  is the universal gas constant,  $T$  the absolute temperature in  $K$ , and 55.5 represents the molar concentration of water in the solution. Fig. 5 shows the dependence of  $C/\theta$  versus  $C$ , the straight line was drawn using the least squares method. The experimental (points) and the theoretical fitting result (line) are plotted in Fig. 5. A very good fit is observed with the regression coefficient up to 0.9999 and the slope is more than unity, which suggests that the experimental data are well described by Langmuir isotherm. The  $K_{ads}$  value may be taken as a measure of the strength of the adsorption forces between the inhibitor molecules and the metal surface. Therefore, there is a phase boundary between the corrosive medium and the surface of mild steel owing to the strong adsorption of inhibitor molecules on the surface of mild steel ( $K_{ads} = 22310 \text{ M}^{-1}$ )[15,18]. The negative value of  $\Delta G^{\circ}_{ads}$  suggests that the adsorption of inhibitor molecules onto steel surface is a spontaneous process[17]. Generally speaking, the adsorption type is regarded as chemisorption if the absolute value of  $\Delta G^{\circ}_{ads}$  is of the order of  $40 \text{ kJ mol}^{-1}$  or higher, while the values less than  $20 \text{ kJ/mol}$  are associated to physisorption process[16,17,20]. In this process, the calculated  $\Delta G^{\circ}_{ads}$  value ( $-35.32 \text{ kJ mol}^{-1}$ ) indicates that the adsorption mechanism of BMI on mild steel in hydrochloric acid is physiochemisorption, which is attribute to the charge sharing or transferring and electrostatic interaction from the inhibitor molecules to the metal surface[28].

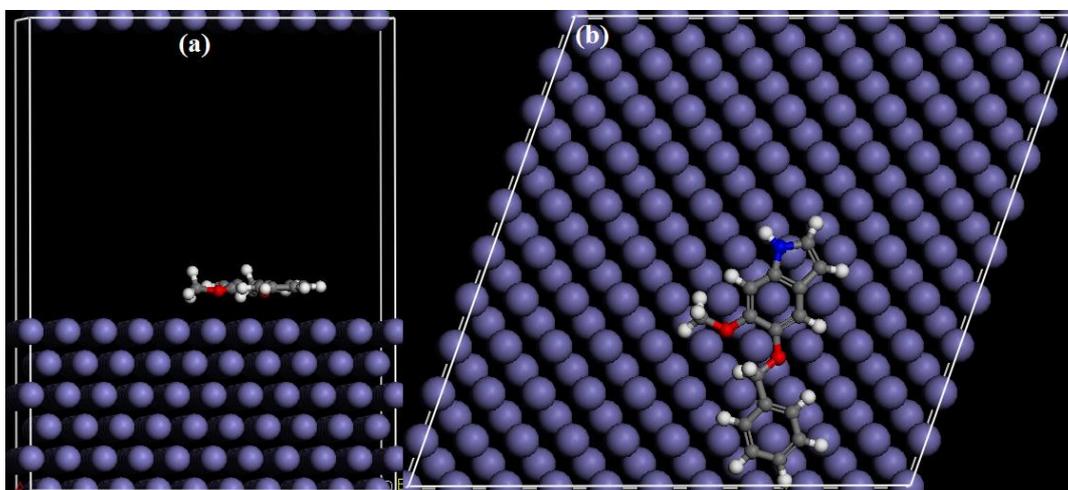
Figure 5: Langmuir adsorption of inhibitor on the MS surface in 1.0 M HCl solution at 303K.



#### Monte Carlo simulation

The molecular dynamics simulation has been broadly used to describe the interaction between metal and inhibitor because it provides some essential parameters such as total energy, adsorption energy, and rigid adsorption energy[24]. In the present study, the Monte Carlo simulation calculation was used to find the lowest energy for the investigated system. The outputs and descriptors calculated by the Monte Carlo simulation, such as the total adsorption, adsorption energy, rigid adsorption and deformation energies are presented in Table 4. Figure 6 represents the most stable low energy configuration for the adsorption of BMI on Fe (1 1 0) surface obtained through the Monte Carlo simulations. It is well known that the ligation capability of a molecule to a metal surface depends on the electronic charge, the chelating or active atoms, i.e. the more negative charge, and the stronger is the binding capability. The investigated inhibitor have different active sites for adsorption on the metal surface. The structures of the adsorbate component were minimized until they satisfied certain specified criteria. As can be seen from Table 4, BMI molecule showed the maximum adsorption energy found during the simulation process which indicates that this molecule has the highest inhibition efficiency, which is in agreement with the experimental observations[22–24].

Figure 6. The most stable low energy configuration for the adsorption of the inhibitor on Fe (1 1 0) surface obtained through the Monte Carlo simulation.(a) side view, (b) top view.



**Table 4. Outputs and descriptors calculated by the Monte Carlo simulation for the lowest adsorption. Configurations of BMI Fe (1 1 0) surface (in kcal/mol).**

System	Total energy	Adsorption energy	Rigid Adsorption energy	Deformation energy	dE <sub>ad</sub> /dN <sub>i</sub> inhibitor
Fe (1 1 0)/BMI	23.163	-154.617	-150.609	-4.007	-154.617

### CONCLUSION

The following conclusion can be drawn from the present study.

- BMI was found to be a better inhibitor of the mild steel corrosion.
- The *PDP* indicate that the inhibitor act as a mixed type. In *EIS* study, the Double layer capacitance,  $C_{dl}$  values of solution with the inhibitor molecules were lower than the blank solution and were found to be decreasing with increasing inhibitor concentration.
- The adsorption of the molecule on mild steel surface followed Langmuir isotherm at tested temperature at all the studied concentrations.
- The inhibitor molecules adsorbed on the metal surface blocking the reaction sites. Higher surface coverage on the metal surface was obtained with higher inhibitor concentrations.
- From Monte Carlo simulation studies, BMI showed highest ability to adsorb on Fe (1 1 0) surface with highest adsorption energy.

### Acknowledgements

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