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Corrosion inhibition potentiality of some benzimidazole derivatives for mild steel in hydrochloric acid: Electrochemical and weight loss studies

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Abstract

The adsorption and inhibition effects of three benzimidazole derivatives (BDD), namely: 2-(2-pyridyl)benzimidazole (PBD), 2-bromo-1*H*-benzimidazole (BrBD), and 2-chloro-benzimidazole (ClBD) on mild steel corrosion in 1 M HCl have been studied by electrochemical and weight loss methods. Results showed that inhibition efficiency increases with concentration and maximum value was obtained at $5 \cdot 10^{-3}$ M concentration. From the results, it is concluded that the BDD inhibited mild steel corrosion in 1 M HCl by adsorbing on the metal surface. Polarization results showed that the BDD act as mixed type inhibitors. The adsorption of BDD onto the mild steel surface was described by the Langmuir adsorption isotherm.

Keywords: *corrosion inhibition, mild steel, EIS, weight loss, benzimidazole derivatives.*

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Introduction

Acid solutions are commonly used for pickling, industrial acid cleaning, acid descaling, and oil-well acidifying processes [1–3]. Because of the aggressiveness of acid solutions, mild steel corrodes severely during these processes, particularly with the use of hydrochloric acid, which results in terrible waste of both resources and money. A corrosion inhibitor is often added to mitigate the corrosion of metal by acid attack [4–7]. Most well-known corrosion inhibitors are organic compounds containing polar groups including nitrogen, sulfur, and/or oxygen atoms and heterocyclic compounds with polar functional groups and conjugated double bonds [8–10]. The inhibiting action of these compounds is due to the adsorption of these compounds to the metal/solution interface. The adsorption process depends upon the nature and surface charge of the metal, the type of aggressive media, the structure of the inhibitor and the nature of its interaction with the metal surface [11–13]. The choice of these compounds is based on molecular structure considerations,

i.e., the number of active centers and type of substituents present in these compounds [14–16].

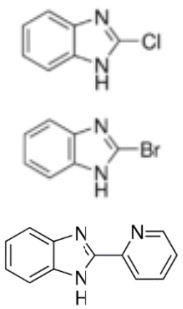
The objective of this work is to investigate the corrosion inhibition properties of three benzimidazole derivatives, namely, 2-(2-pyridyl)benzimidazole (PBD), 2-bromo-1*H*-benzimidazole (BrBD), and 2-chlorobenzimidazole (ClBD) on mild steel in 1 M HCl using electrochemical techniques and weight loss studies.

Experiment

Electrodes, chemicals and test solution

Corrosion tests have been performed, using the gravimetric and electrochemical measurements, on electrodes cut from sheets of mild 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 BDD used in this investigates were varied from $5\cdot10^{-4}$ to $5\cdot10^{-3}$ M. The inhibitors molecule used in this paper was purchased from Sigma–Aldrich and have the structure presented in Figure 1. As can be seen, they have different active groups, which can act as adsorption centers.



2-Chlorobenzimidazole (ClBD)

2-Bromo-1H-benzimidazole (BrBD)

2-(2-Pyridyl)benzimidazole (PBD)

Figure 1. Chemical structure of inhibitors.

Gravimetric measurements

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 $2.5\times2.0\times0.2$ 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 BDD at temperature equal to 303 K maintained by a water thermostat for 6 h as immersion time. The gravimetric tests were performed in triplicate at the same conditions.

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

$$C_R = \frac{w}{St}, \tag{1}$$

$$\eta_{wt}\% = \frac{C_R^0 - C_R}{C_R^0} \times 100, \tag{2}$$

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 BDD inhibitor, respectively.

Electrochemical tests

The potentiodynamic polarization curves were conducted using an electrochemical measurement system PGZ 100 Potentiostat/Galvanostat controlled by a PC supported by the Voltamaster 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 system stabilization 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^{-1}. The temperature is thermostatically controlled at desired temperature ± 1 K.The percentage protection efficiency (η_{PDP}%) is defined as:

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

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 5 mV 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 (η_{EIS}%) is can be calculated by the value of the charge transfer resistance (R_{ct})

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

where R_{ct} and R_{ct}^{0} are the polarization resistance of uninhibited and inhibited solutions, respectively.

Results and discussion

Weight loss study

Weight loss measurements were carried out in 1.0 M HCl in the absence and presence of different concentrations of BDD at 303 K after 6 h immersion period. Table 1 presents the corrosion rate, inhibition efficiency (η_{wl}%) for benzimidazole derivatives at different concentrations. The results show that three compounds inhibit the corrosion of mild steel in 1.0 M HCl solutions given that the corrosion rate was reduced in the presence of the BDD compared to the blank solution. The corrosion rate was found to depend on the concentration of the BDD. Inspection of the table revealed a decrease in corrosion rate as the concentration of the BDD increased. It could be also observed from the Table 1 that inhibition efficiency increased with increase in the concentration of the BDD. It is noted that the maximum inhibition efficiency obtained for PBD, BrBD and ClBD are 97%, 95% and 93% respectively at 303 K with the highest concentration ($5 \cdot 10^{-3}$ M) of the BDD studied. This indicates that BDD are better corrosion inhibitors. The inhibition behavior of these BDD for mild steel corrosion in the acidic medium can be attributed to the adsorption of the components on the mild steel surface, which retards the dissolution of the metal by blocking its active corrosion sites [17, 18]. Consequently, the corrosion rate is reduced and the inhibition efficiency is increased as the BDD concentration is increased.

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

Inhibitors	Concentration (M)	C_R (mg cm^{-2} h^{-1})	η_{wl} (%)	Θ
Blank	1.0	1.135	–	–
PBD	$5 \cdot 10^{-3}$	0.0320	97.18	0.9718
	$1 \cdot 10^{-3}$	0.0671	94.08	0.9408
	$5 \cdot 10^{-4}$	0.0984	91.33	0.9133
BrBD	$5 \cdot 10^{-3}$	0.0519	95.43	0.9543
	$1 \cdot 10^{-3}$	0.0879	92.25	0.9225
	$5 \cdot 10^{-4}$	0.1299	88.55	0.8855
ClBD	$5 \cdot 10^{-3}$	0.0705	93.78	0.9378
	$1 \cdot 10^{-3}$	0.1122	90.11	0.9011
	$5 \cdot 10^{-4}$	0.1457	87.16	0.8716

Polarization results

The potentiodynamic polarization curves for mild steel in 1 M HCl solution at 303 K in the absence and presence of various concentrations of the studied BDD are presented in Figure 2. The curves are shifted to lower current regions in the presence of inhibitors showing that the studied benzimidazole derivatives inhibit the corrosion reaction. It is observed that the polarization curve for PBD (at $5 \cdot 10^{-3}$ M) appeared at lower current region than those of BrBD and ClBD.

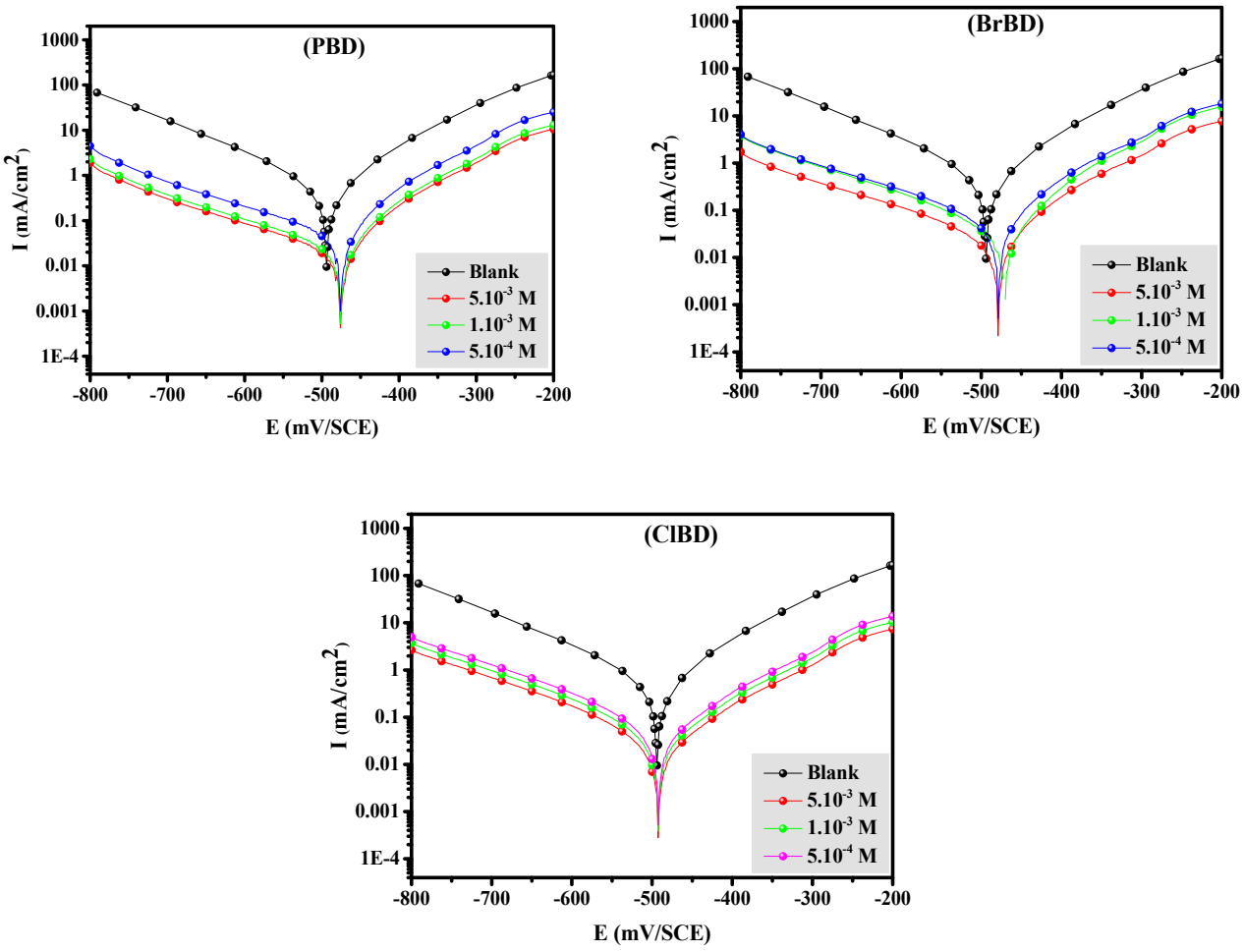


Figure 2. Polarisation curves of MS in 1 M HCl for various concentrations of BDD at 303 K.

The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential (E_{corr}) to obtain corrosion current density (i_{corr}). The values of electrochemical kinetic parameters obtained from the Tafel fitting of the polarization curves are presented in Table 2. The shift in E_{corr} values of the inhibited systems compared to the blank solutions is less than 80 mV, suggesting that the studied benzimidazole derivatives are mixed type inhibitors [19–21]. That is, they inhibit both the anodic

dissolution of mild steel and the cathodic H^+ ion reduction. The cathodic Tafel lines show similar shape either in presence or absence of BDD. It indicates that the mechanism of the cathodic reaction does not change in presence of the inhibitor and the inhibition action is achieved by simple blocking of the iron surface [22, 23]. The inhibition efficiency ($\eta_{PDP}\%$) increases with increase in concentration for the three BDD with PBD showing the highest values of $\eta_{PDP}\%$. This implies that the studied BDD inhibit mild steel corrosion in 1 M HCl and the strength of their inhibition potential increases with the presence of Cl, Br and pyridyl groups in its structure in the following trend: pyridyl > Br > Cl.

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

Inhibitor	Concentration (M)	$-E_{corr}$ (mV/SCE)	I_{corr} (μA cm^{-2})	η_{PDP} (%)	Θ
Blank	–	496	564.0	–	–
PBD	$5\cdot10^{-3}$	477	14.21	97.48	0.9748
	$1\cdot10^{-3}$	475	26.32	95.33	0.9533
	$5\cdot10^{-4}$	476	47.98	91.49	0.9149
BrBD	$5\cdot10^{-3}$	481	28.24	94.99	0.9499
	$1\cdot10^{-3}$	473	52.73	90.65	0.9065
	$5\cdot10^{-4}$	482	73.33	86.99	0.8699
ClBD	$5\cdot10^{-3}$	491	39.84	92.93	0.9293
	$1\cdot10^{-3}$	493	62.42	88.93	0.8893
	$5\cdot10^{-4}$	490	78.54	86.07	0.8607

EIS study

Electrochemical impedance measurements were undertaken to provide information on the kinetics of the electrochemical processes at the mild steel/acid interface and how this is modified by the presence of inhibitors. Nyquist plots for mild steel corrosion in 1 M HCl solution in the absence and presence of different concentrations ($5\cdot10^{-4}$ – $5\cdot10^{-3}$ M) of the inhibitors PBD, BrBD and ClBD are given in Figure 3, respectively. The Nyquist plots show single semicircles for all systems over the frequency range studied, corresponding to one time constant [24–26].

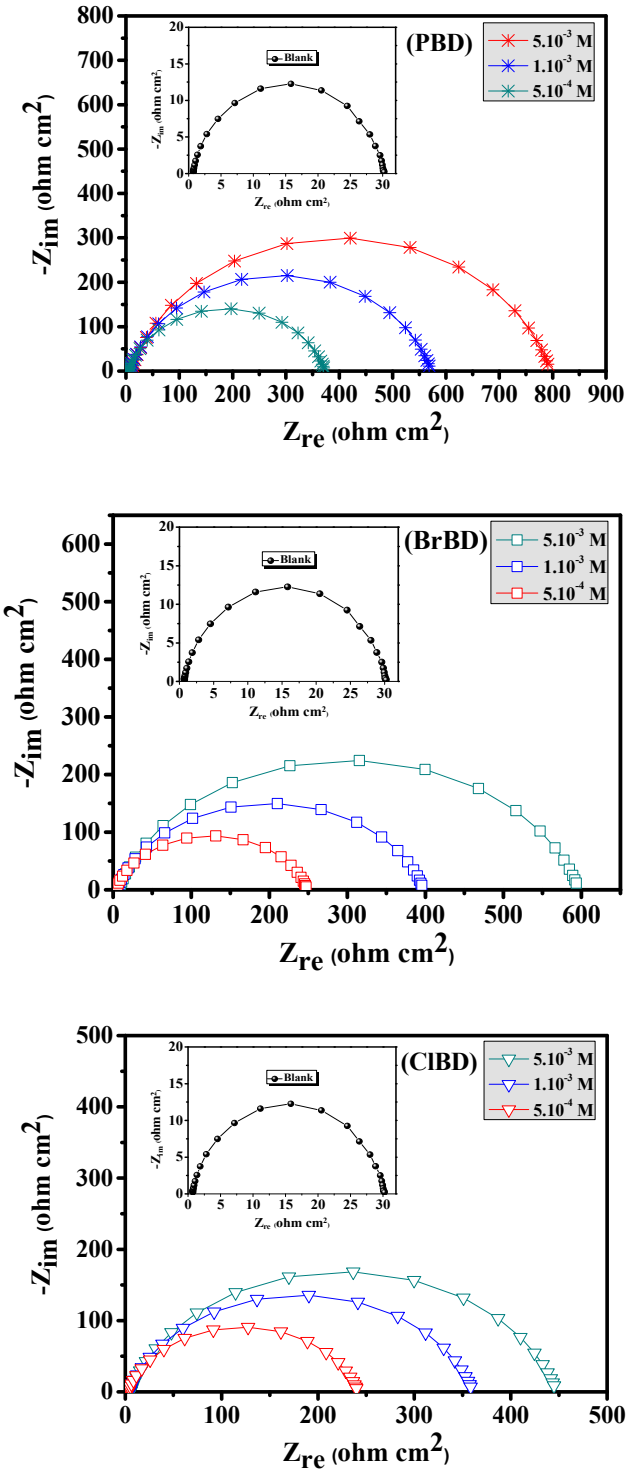


Figure 3. Nyquist curves for mild steel in 1 M HCl for selected concentrations of BDD at 303K.

The impedance spectra were analyzed by fitting to the equivalent circuit model shown in Figure 4, which has been used previously to adequately model the mild steel/acid interface [27, 28], 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 [29, 30]. The impedance of this element is frequency-dependent and can be calculated using the Eq. (5):

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

where Q is the CPE constant (in Ω^{-1} S^n cm^{-2}), ω 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 [31, 32]. In addition, the double layer capacitances, C_{dl}, for a circuit including a CPE were calculated by using the following Eq. (6):

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

The fitted parameters along with percentage inhibition efficiencies, $(\eta_{EIS}\%)$ are tabulated in Table 3. For all the inhibitors, diameter of the capacitive loop is seen to increase gradually with concentration, which is manifested in progressively increasing R_{ct} values with concomitant decrease in values of the double layer capacitance, C_{dl}. This suggests that the extent of adsorption increases with concentration of the inhibitors and thereby provides better barrier towards charge transfer reactions at the metal–solution interface [23, 31, 32]. Percentage inhibition efficiency in terms of R_{ct} values $(\eta_{EIS}\%)$ are found to follow the order PBD > BrBD > ClBD; *i.e.*, the same trend as observed from polarization experiment. It also supports the fact that presence of pyridine group provides better adsorption potentiality for PBD, than those for Br and Cl atoms in BrBD and ClBD, respectively.

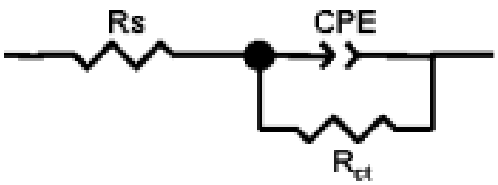


Figure 4. Equivalent electrical circuit corresponding to the corrosion process on the carbon steel in hydrochloric acid.

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

Inhibitor	Concentration (M)	R_{ct} (Ω cm^2)	n	$Q\times10^{-4}$ ($s^n\ \Omega^{-1}cm^{-2}$)	C_{dl} (μF cm^{-2})	η_{EIS} (%)	Θ
Blank	1.0	29.35	0.910	1.7610	91.6	–	–
PBD	$5\cdot10^{-3}$	786.6	0.901	0.1776	11.10	96.26	0.9626
	$1\cdot10^{-3}$	565.4	0.879	0.2812	15.90	94.80	0.9480
	$5\cdot10^{-4}$	368.7	0.853	0.3943	19.01	92.03	0.9203
BrBD	$5\cdot10^{-3}$	590	0.845	0.2868	13.57	95.02	0.9502
	$1\cdot10^{-3}$	393.3	0.883	0.4032	23.28	92.53	0.9253
	$5\cdot10^{-4}$	245.8	0.894	0.5371	32.15	88.05	0.8805
ClBD	$5\cdot10^{-3}$	442.5	0.904	0.3342	21.36	93.36	0.9336
	$1\cdot10^{-3}$	356.4	0.874	0.4521	24.93	91.76	0.9176
	$5\cdot10^{-4}$	238.4	0.854	0.6778	33.48	87.68	0.8768

Adsorption isotherm

Results so far obtained indicate that the primary mode of interaction of PBD, BrBD and ClBD on steel surface is by adsorption. The adsorption of organic inhibitor molecules from the aqueous solution can be considered as a quasi-substitution process between the organic compounds in the aqueous phase [$Org_{(sol)}$] and water molecules associated with the metallic surface [$H_2O_{(ads)}$] as represented by the following equilibrium [33, 34]:

$$Org_{(sol)} + xH_2O_{(ads)} \leftrightarrow Org_{(ads)} + xH_2O_{(sol)},$$

where x is the number of water molecules replaced by one organic molecule. In this situation, the adsorption of benzimidazole derivatives was accompanied by desorption of water molecules from the mild steel surface. The degree of surface coverage (Θ) was evaluated from the weight loss measurements. In 1 M HCl, BDD adsorption follows the Langmuir isotherm (Figure 5) as per Eq.7 [35]:

$$\frac{C}{\Theta} = \frac{1}{K_{ads}} + C, \tag{7}$$

where C is the concentration of the inhibitor, K_{ads} is the equilibrium constant of adsorption and Θ 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 (ΔG^0_{ads}) of the inhibitor molecules by the following Eq. 8:

$$K_{ads} = \frac{1}{55.5}\exp(\frac{-\Delta G^0_{ads}}{RT}), \quad (8)$$

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. Calculated values of K_{ads} and ΔG^0_{ads} are listed in Table 4. The negative values of ΔG^0_{ads} reveal the spontaneity of adsorption process [36, 37]. In general, values of ΔG^0_{ads} up to –20 kJ/mol are compatible with physisorption and those which are more negative than –40 kJ/mol involve chemisorption [38, 39]. The calculated ΔG^0_{ads} values for PBD, BrBD and ClBD were found to be –35.67, –35.31 and −35.09, respectively, at temperatures of 303 K, these values were between the threshold values for physical adsorption and chemical adsorption, indicating that the adsorption process of these inhibitors at mild steel surface involves both the physical as well as chemical adsorption [40, 41].

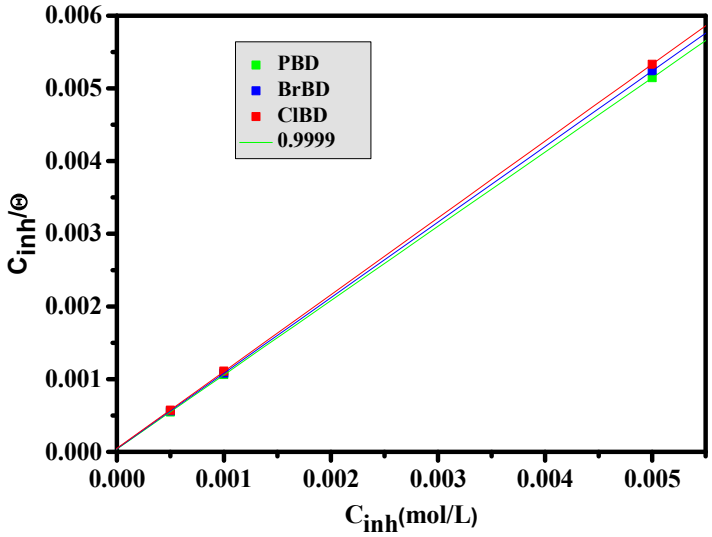


Figure 5. Langmuir adsorption of inhibitor on the MS surface in 1.0 M HCl solution at 303K.

Table 4. Adsorption parameters of inhibitor for MS corrosion in 1M HCl at 303 K

Inhibitor	Slope	K_{ads} (M^{-1})	ΔG^0_{ads} (kJ/mol)
PBD	1.02	25596	–35.67
BrBD	1.03	22164	–35.31
ClBD	1.05	20384	–35.09

Conclusion

The corrosion inhibition of benzimidazole compounds PBD, BrBD and ClBD for mild steel in 1 M HCl was evaluated using chemical and electrochemical measurements. The obtained results showed that these compounds have good inhibition efficiency, which increases with the inhibitor concentration and follows the order: PBD > BrBD > ClBD. The value of adsorption equilibrium constant (K) suggested that these derivatives are strongly adsorbed on the mild steel surface according to Langmuir adsorption isotherm. Potentiodynamic polarization study shows that studied inhibitors are a mixed type inhibitors.

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