Int. J. Electrochem. Sci., 9 **(2014)** 1840 - 1853

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Inhibition and Adsorptive Behavior of Synthesized 1, 4-Bis (2-Benzimidazolyl) Benzene on Mild Steel in 3 M HCl Solution

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Received: 7 November 2013 / *Accepted:* 28 December 2013 / *Published:* 2 February 2014

Weight loss measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves were used to assess the inhibition and adsorptive behavior of 1, 4-Bis (2-Benzimidazolyl) Benzene (BBMB) on mild steel in 3 M HCl solution at 303-333 K. Results obtained show that BBMB acts as a good inhibitor on mild steel by reducing anodic dissolution and retarding the hydrogen evolution reaction. With the increase in temperature, corrosion current density of mild steel in blank solution increases, however, its increase is lower in the presence of BBMB than that in blank solution. The inhibition efficiency was found to increase with the increase in BBMB concentration and the rise in temperature. The adsorption of the BBMB on the mild steel surface obeyed Langmuir adsorption isotherm model. Thermodynamic adsorption parameters show that BBMB is absorbed on mild steel surface in 3 M HCl solution by a spontaneous endothermic process accompanied by the negative increase in entropy and its adsorption mechanism is combination of physisorption and chemisorption.

Keywords: Corrosion inhibition; Mild Steel; Electrochemical experiments; Langmuir adsorption

1. INTRODUCTION

In chemical industries and oil field, aggressive acids (especially HCl and H_2SO_4) are frequently used for acidification and the removal of rust from iron and steel which leads to the corrosion of equipments. In order to avoid the equipments corroded, the inhibitors are always added to the pickling bath. Among the inhibitors, a large number of organic compounds containing heteroatoms (N, O, P, S) and multiple bonds in their molecular structures have been proved as effective corrosion inhibitors for mild steel in acidic solutions [1-7]. It has been reported that heterocyclic organic compounds have better inhibition effect in acidic media [8-21]. It is generally explained that heterocyclic compounds exert good inhibition by the formation of a physisorption and/or chemisorption film barrier on steel surface, through heteroatoms, as well as those with triple or double bonds or conjugated π bonds or aromatic rings in their molecular structures. In addition, inhibiting effect of heterocyclic compounds always increases with the number of aromatic systems and high electronegative heteroatoms in the molecule [16]. Physical adsorption involves electrostatic attractive forces between the electric charge at metal/solution interface and ionic charges or dipoles on the adsorbed species. Whereas, chemical adsorption involves electron pairs sharing or electron transfer from the inhibitor molecules to the metal surface, thus resulting in a coordinate bond formation. As a matter of fact, electron transfer is normally reported for transition metals having vacant electron orbital with low energy. Chemical adsorption generally is characterized by more negative adsorption free energy than physical adsorption. This family of N-heterocyclic compounds can create excellent inhibition properties in acidic solution and can be strongly adsorbed onto the steel surface.

The aim of this paper was to investigate a N-heterocyclic compound namely of 1,4-bis (benzimidazolyl) benzene (BBMB) as a corrosion inhibitor for mild steel in 3 M HCl media through weight loss measurements, electrochemical experiments.

2. EXPERIMENTAL

2.1. Material

Commercial mild steel strips of the following composition 0.15% C, 0.06% Si, 0.32% Mn, 0.05% P and the remainder Fe were used for the present study. Specimens of size 20 mm × 20 mm × 0.5 mm were used for weight loss measurements. For electrochemical measurements, the mild steel working electrode was a cylindrical rod with the length 1 cm and sealed with epoxy resin, having an exposed surface area of 0.785 cm^2. Before experiments, the specimens were polished with SiC paper (successively 100-800 grits), degreased with acetone and washed thoroughly with double distilled water, dried and kept in desiccators. The corrosive solution of 3 M HCl was prepared by the dilution of analytical grade 37% HCl with double distilled water.

2.2. Weight loss measurements

After weighing accurately by digital balance with sensitivity of ±0.0001g, mild steel specimens were immersed in triplicate in 250 mL of 3 M HCl solution without and with addition of different concentrations of inhibitor (concentration ranged from 1.6×10^{-4} to 16×10^{-4} mol L^{-1}). After 5 h, the test specimens were taken out, rinsed thoroughly with distilled water to remove the corrosion product, dried and reweighed accurately and the mean value of weight loss was reported. The experiment temperature (303-333K) was also carried out for a period of 5 h using water circulated Ultra thermostat.

The inhibitive property of the compound is expressed in terms of inhibition efficiency (η%) and is determined by following equations[22].

$$\rho = \frac{\Delta W}{At} \quad (1)$$

where ρ is the corrosion rate, ΔW is the mean weight loss of the mild steel before and after corrosion in gramme, A is the corrosion area of the mild steel in cm^2 and t is the corrosion time of the mild steel in hour.

$$\eta\% = \frac{\rho_1 - \rho_2}{\rho_1} \times 100 \quad (2)$$

Where ρ_1 and ρ_2 are the corrosion rates of the mild steel without and with addition of inhibitor, respectively.

The degree of surface coverage (θ) was calculated by the following equation:

$$\theta = \frac{\rho_1 - \rho_2}{\rho_1} \quad (3)$$

Where ρ_1 and ρ_2 are the corrosion rates of the mild steel without and with addition of inhibitor, respectively.

2.3. Electrochemical experiments

Electrochemical experiments were carried out using ParSTAT2273 (Princeton Applied Research). Three conventional compartment cell with saturated calomel electrode (SCE) as reference electrode and all presented potential values were referred to this electrode, platinum sheet (2 cm^2) as auxiliary electrode and mild steel as working electrode was used in 3 M HCl solution without and with inhibitor concentration ranging from 1.6×10^{-4} to 16×10^{-4} mol L^{-1}. The working electrode was allowed for 30 min in the test solution for stabilization of corrosion potential before recording electrochemical data. All the experiments were conducted at 303K and each value is the mean of triplicate experiments.

The electrochemical impedance spectroscopy (EIS) measurements were performed at the open-circuit potential by a perturbation signal of 10 mV and over the frequency range 100 kHz–0.01 Hz. The electrochemical impedance spectroscopy was analyzed employing the Z_{View} software.

For potentiodynamic polarization measurement, the potential was recorded by changing the potential automatically from -150 to +350 mV versus open circuit potential (OCP) with a sweep rate of 0.5 mV/s from cathodic to anodic direction. Potentiodynamic polarization data were analyzed by means of C_{view}.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

The corrosion of mild steel in 3 M HCl solution without and with various concentrations of BBMB was investigated by weight loss measurements. The percentage inhibition efficiencies (η %) and the corrosion rate (ρ) have been given in Table 1 at 303-333K. In table 1, the corrosion rate of mild steel in 3 M HCl solution in presence of different concentrations of BBMB was reduced and the lowest value obtained at the highest concentration (16×10^{-4} mol L^{-1}) of BBMB used at all the temperatures studied. The corrosion rate decreases with increasing of BBMB concentration corresponding to increase in inhibition efficiency at the same temperature. The inhibition efficiency reaches 96.0% when the concentration of BBMB is 16×10^{-4} mol L^{-1}at 333 K. This could be ascribed to the adsorption of BBMB on the mild steel surface leading to corrosion inhibition effect. Corrosion inhibition depends on the displacement of already adsorbed water molecules by BBMB molecules leading to specific adsorption of BBMB on the mild steel surface [23]. This trend may result from the fact that the adsorption amount and the coverage of inhibitor on the mild steel surface increase with increasing inhibitor concentration. Thereby, the mild steel surface is effectively separated from the corrosion medium by the inhibitor adsorption film [24, 25].

Table 1. Corrosion parameters for mild steel in 3 M HCl solution without and with different concentrations of BBMB at 303-333 K.

T	C	ρ	η	θ
/K	$/\times10^{-4}$ mol L^{-1}	/g cm^{-2} h^{-1}	/%	
303	blank	0.00034	-	-
	1.6	0.00016	52.9	0.53
	3.2	0.00014	58.8	0.59
	6.4	0.00011	68.1	0.68
	9.6	0.000098	71.1	0.71
	16	0.000085	75.0	0.75
313	blank	0.00071	-	-
	1.6	0.00022	69.0	0.69
	3.2	0.00019	73.2	0.73
	6.4	0.00016	77.2	0.77
	9.6	0.00012	83.1	0.83
	16	0.000085	88.0	0.88
323	blank	0.0015	-	-
	1.6	0.00029	80.7	0.81
	3.2	0.00023	84.7	0.85
	6.4	0.00019	87.3	0.87
	9.6	0.00015	90.0	0.90
	16	0.00012	92.0	0.92
333	blank	0.0043	-	-
	1.6	0.00038	91.2	0.91
	3.2	0.00032	92.6	0.93
	6.4	0.00025	94.2	0.94
	9.6	0.00021	95.1	0.95
	16	0.00017	96.0	0.96

Table 1 also revealed that corrosion rate of mild steel and the inhibition efficiency of BBMB increases with the rise in temperature at the same BBMB concentration. The results suggest that there should be a strong chemical bond between the BBMB molecules and the mild steel surface. Similar result was also reported by Bouklah [25]. Here, it is worth to emphasize that the high value of η was obtained merely on the basis of more strong increase of corrosion rate value with increasing temperature in uninhibited solution than that in inhibited solution.

3.2. Electrochemical impedance spectroscopy (EIS) measurements

Electrochemical impedance spectroscopy (EIS) is an effective method for corrosion studies of metallic materials. The effect of BBMB concentration on the impedance spectra of mild steel in 3 M HCl solutions at 303 K is recorded in Fig. 1(Nyquist plots). It is clear to see that the impedance spectra are significantly changed with addition of different BBMB concentration. From the Nyquist plots, it was also observed that, even the presence of BBMB does not alter the style of impedance plots, thus indicating the addition of BBMB does not change the mechanism for the dissolution of mild steel in 3 M HCl solution [26-28].

The impedance diagrams show only one capacitive loop represented by slightly depressed semicircle which indicates that the corrosion of mild steel in 3 M HCl solution is mainly controlled by charge transfer process and formation of a protective layer on the mild steel surface. The diameter of the capacitive loop increases with the increase of BBMB concentration proposing that the formed inhibitive film was strengthened by the addition of BBMB [29]. The depressed semicircles are generally attributed to the frequency dispersion as well as roughness and inhomogeneities of solid surface, and mass transport process [30], distribution of the active sites, adsorption of inhibitors [31-35].

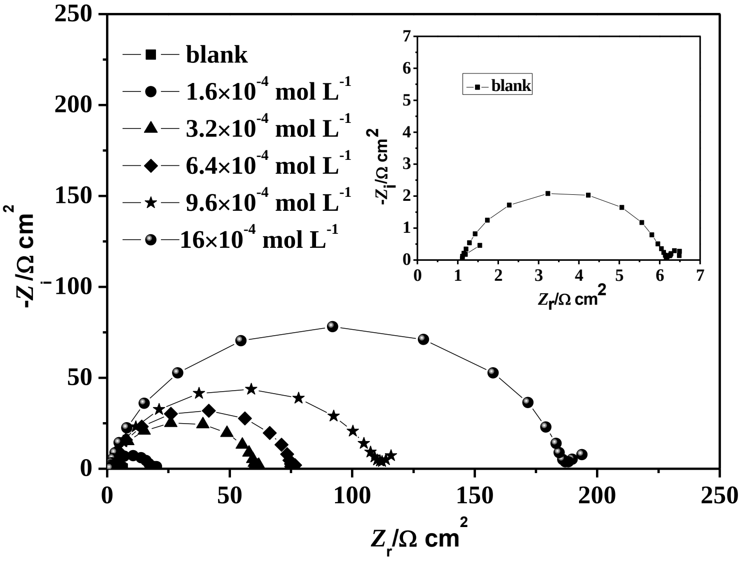

Figure 1. Nyquist plots for the mild steel in absence and presence of different concentrations of BBMB at 303 K.

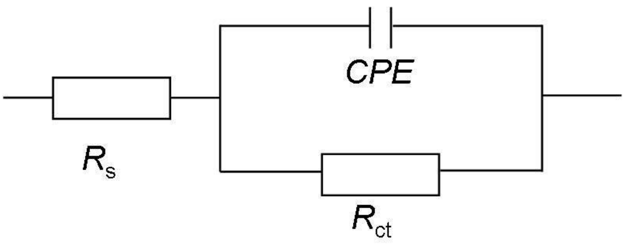

Figure 2. The electrochemical equivalent circuit used to fit the impedance measurements.

Therefore, a constant phase element *CPE* (*Q*) is used to replace a capacitive element to acquire a more accurate fit of experimental data. Fig. 2 displays the equivalent circuit, which consists of a solution resistance R_s, the constant phase element *CPE* (*Q*) and the charge transfer resistance R_{ct}. The impedance of *CPE* is described as the mathematical expression given below [36-37]

$$Z_{\mathrm{CPE}} = \frac{1}{Y_0} \bullet \frac{1}{(J\omega)^{\mathrm{n}}} \qquad (4)$$

Where Y_0 is the magnitude of the *CPE, j* is the imaginary unit, ω is the angular frequency and *n* is the phase shift.

The fitted impedance parameters derived from Nyquist diagrams and inhibition efficiency are listed in Table 2. Data in Table 2 shows that additional BBMB inhibits the corrosion of mild steel in 3 M HCl solution. The inhibitive efficiency increased with the studied inhibitor concentration increasing. The inhibition efficiency is calculated by the equation [38]:

$$\eta(EIS)\% = \frac{R_{\mathrm{ct}} - R_{\mathrm{ct}}^0}{R_{\mathrm{ct}}} \times 100 \qquad (5)$$

where $R_{ct}{}^0$and R_{ct} are the charge transfer resistance values of mild steel in absence and presence of different concentration of BBMB in 3 M HCl solution, respectively. By increasing the inhibitor concentration *Q* values decrease but the R_{ct} values and inhibition efficiency increase. The increase in the charge transfer resistance values with increasing inhibitor concentration suggests the formation of a protective layer on the mild steel electrode surface. This protective layer behaves as a hindrance for mass and charge transfer [39-40].

The decrease in the *Q* value is due to the adsorption of BBMB molecules on the mild steel surface, which displace the water molecules and other species already adsorbed on the mild steel surface [41]. The adsorption of the inhibitor molecules on mild steel surface can occur either directly on the basis of interaction of protonated BBMB with originally adsorbed chloride ions or donor–acceptor interaction between the π electrons (of the benzimidazole ring and benzene ring) and the vacant d-orbitals of iron atoms as proposed. The inhibitive efficiencies calculated from EIS results show the same trend as those obtained from weight loss measurements.

Table 2. Impedance parameters for mild steel in 3 M HCl solution in absence and presence of different concentrations of BBMB at 303 K.

C	R_s	$CPE(Q)$	n	R_{ct}	η
/ $\times 10^{-4}$ mol L^{-1}	/ Ω cm^2	/ μF cm^{-2}		/ Ω cm^2	/ %
blank	1.2	302	0.93	5	
1.6	1.2	192	0.91	17	70.6
3.2	1.3	89	0.9	59	91.5
6.4	1.4	74	0.91	74	93.2
9.6	1.4	63	0.88	108	95.4
16	1.4	36	0.9	185	97.3

According to the above results, the inhibition efficiency of BBMB on mild steel in 3 M HCl at 298 K is lower than that at all of the studied temperatures. Comparing them with our previous work [26], it can be seen that BBMB in 3 M HCl has a worse inhibition effect on mild steel than in 0.5 M HCl. The possible reason is that with the increase of HCl concentration, the corrosion rate increased in inhibited HCl solution is more than in uninhibited HCl solution.

3.3. Potentiodynamic polarization curves

Potentiodynamic polarization curves method is another useful and fast method for inhibitors study. The potentiodynamic polarization curves are shown Fig. 3. Various electrochemical parameters obtained by extrapolation and percentage inhibition efficiency (η) calculated by equation (6) are given in Table 3.

$$\eta\% = \left(\frac{i_{\mathrm{corr}} - i'_{\mathrm{corr}}}{i_{\mathrm{corr}}}\right) \times 100 \qquad (6)$$

where i_{corr} and i'_{corr} are corrosion current densities without and with different concentration of BBMB, respectively.

In acidic medium, the cathodic process is the discharge of hydrogen ions to release hydrogen gas, and the anodic process is the dissolution of metal and passage of metal ions from the metal surface into the medium. The added inhibitor may affect either the cathodic or the anodic process, or both [42]. In Fig.3, the addition of BBMB shows no change of the nature of the curve on increasing the concentration of BBMB indicating that the BBMB suppresses the corrosion process without changing the corrosion mechanism of mild steel in 3M HCl medium [43]. Both anodic and cathodic polarization curves shifted toward lower current density in the presence of BBMB which may be due to an inhibition protection of the BBMB adsorption layer on the mild steel surface, indicating BBMB as a mixed-type inhibitor [1, 44].

The minor shift in corrosion potential (E) after addition of BBMB also supports the mixed nature of BBMB [45].

In Table 3, it is clear to see that by the increasing BBMB concentration the corrosion current density (i_{corr}) value decrease greatly because of the formation of BBMB adsorption film on the mild steel surface, while η values increases, and the maximum η % is up to 96.0% at 16×10^{-4} mol L^{-1}. Furthermore, the inhibition efficiencies obtained from potentiodynamic polarization curves, EIS and weight loss method are in good agreement. The small difference comparison to EIS measurements may be caused by environment conditions and state of the metal surface.

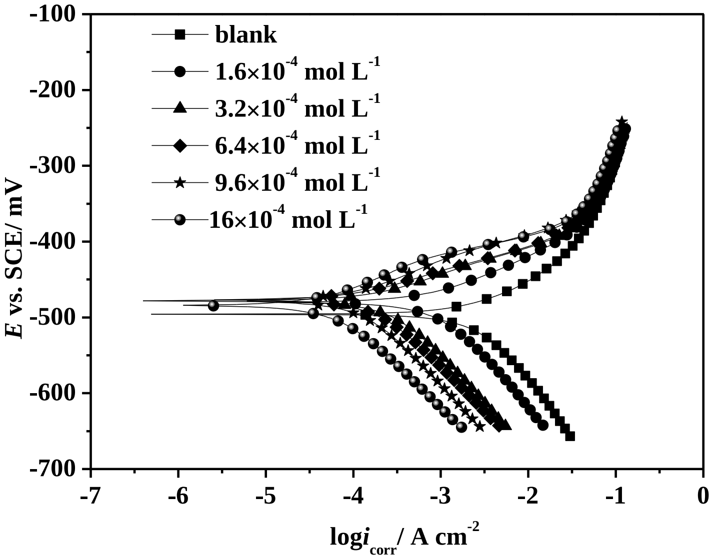

Figure 3. Potentiodynamic polarization curves for corrosion of mild steel in 3 M HCl solution in the absence and presence of different concentrations of BBMB at 303 K.

3.4. Adsorption considerations

The mechanism of corrosion inhibition may be illustrated on the basis of adsorption isotherm. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of BBMB must be calculated. In this study, the degree of surface coverage values (θ) for various concentrations of BBMB in 3 M HCl solution have been obtained from Table 1. Attempts were made to fit the data to different isotherms, including Langmuir, Bockris–Swinkles, Temkin, Flory-Huggins and Frumkin. Among the isotherms, the best fit is the Langmuir isotherm. According to Langmuir adsorption isotherm, the relation of inhibitor concentration(C) and surface coverage (θ) is described by equation (7) [46]:

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

where C is the inhibitor concentration(mol L^{-1}), θ is the surface coverage, K_{ads} is the adsorption equilibrium constant(L mol^{-1}). K_{ads} is related to the Gibbs free energy of adsorption, ΔG_{ads} (kJ mol^{-1}) as [47]:

$$K_{\mathrm{ads}}=\frac{1}{C_{\mathrm{solvent}}}\exp\left(\frac{-\Delta G_{\mathrm{ads}}}{RT}\right) \qquad (8)$$

where *R* (8.314 J mol^{-1} K^{-1}) is the molar gas constant, *T* (K) is the absolute temperature, and $C_{solvent}$ is the concentration of the solvent, which in this case is water (C_{H2O} = 55.5 mol L^{-1}).

Fig.4 shows the linear plots of C/θ versus *C* were obtained for the different temperatures indicating that the adsorption of BBMB obeyed Langmuir isotherm. The various adsorption parameters obtained by fitting method from this isotherm are given in Table 4. It is seen from the Table 4 that the correlation coefficient (*r*=0.99921, 0.99699, 0.99964, 0.99995, respectively) demonstrates that adsorption of BBMB on mild steel follows this isotherm and supposes that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species [48]. According to Eq. (7), K_{ads} can be calculated from intercept of the plot of C/θ vs. *C*. With the above equation (8), ΔG_{ads} can be calculated from K_{ads} and listed in Table 4 [48-50].

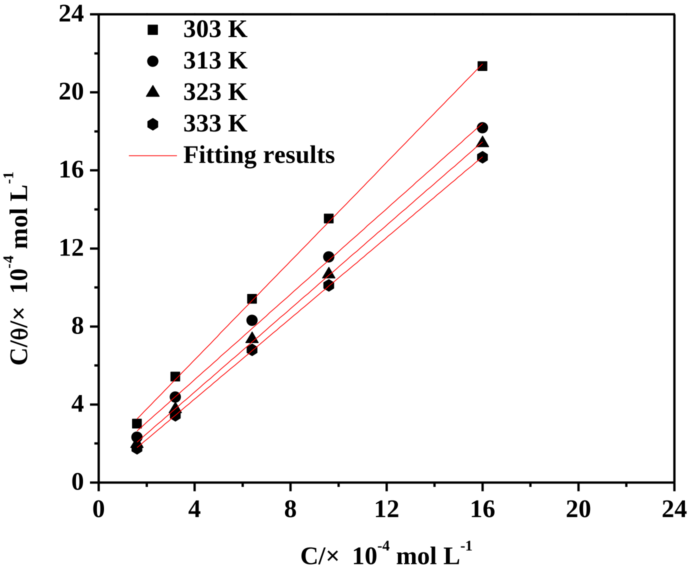

Figure 4. Langmuir adsorption isotherm model for mild steel in 3 M HCl solution containing BBMB at different temperatures.

It can be seen from Table 4 that the standard adsorption equilibrium constant (K_{ads}) increases with temperature, suggesting that the elevated temperature facilitates the adsorption of BBMB, hence, the adsorption of the inhibitor increases with the increasing of temperature. The high value of K_{ads} indicates that the BBMB inhibitor possesses strong chemisorption ability onto the mild steel surface. The calculated ΔG_{ads} are negative in all temperatures and lies between -42.1 and -32.8 kJ mol^{-1}. The negative values of ΔG_{ads} signify that the inhibitor is spontaneously adsorbed onto the metal surface [54]. Normally, the magnitude of ΔG_{ads} around −20 kJ mol^{-1} or less negative is assumed for electrostatic attraction between inhibitor and the charged metal surface (i.e., physisorption). Those around−40 kJ mol^{-1} or more negative are indication of charge sharing or transferring from inhibitive species to the metal surface to form a coordinate bond (i.e., chemisorption) [9, 14]. The calculated values of ΔG_{ads} decreased with an increase in temperature, and all the values of ΔG_{ads} are more negative than -20 kJ mol^{-1} or near -40 kJ mol^{-1} which suggests that the adsorption mechanism of

BBMB on mild steel in 3 M HCl solution is not merely physisorption or chemisorption, and it comprises a comprehensive adsorption (physical and chemical adsorption) for the similar values [51-52].

Table 4. Some parameters from Langmuir isotherm model for mild steel in 3 M HCl solution at different temperatures.

T	slope	intercept	r	K_{ads}	$-\Delta G_{\text{ads}}$
/K		$/\times 10^{-4}$ mol L^{-1}		$/\times 10^{4}$ L mol^{-1}	/kJ mol^{-1}
303	1.06	1.24	0.99921	0.81	32.8
313	1.09	0.90	0.99699	1.11	34.7
323	1.07	0.37	0.99964	2.73	38.2
333	1.03	0.14	0.99995	7.23	42.1

3.5. Effect of temperature and activation parameters

Arrhenius equation (Eq. (9)) was used to obtain the thermodynamic parameters for the dissolution of mild steel in 3 M HCl solution in presence and absence of BBMB.

$$\ln \rho = \ln A - \frac{Ea}{RT} \qquad (9)$$

where ρ is the corrosion rate (g cm^{-2} h^{-1}) at all cases, A is the pre-exponential factor, E_a is the apparent activation energy (kJ mol^{-1}), R is the molar gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K).

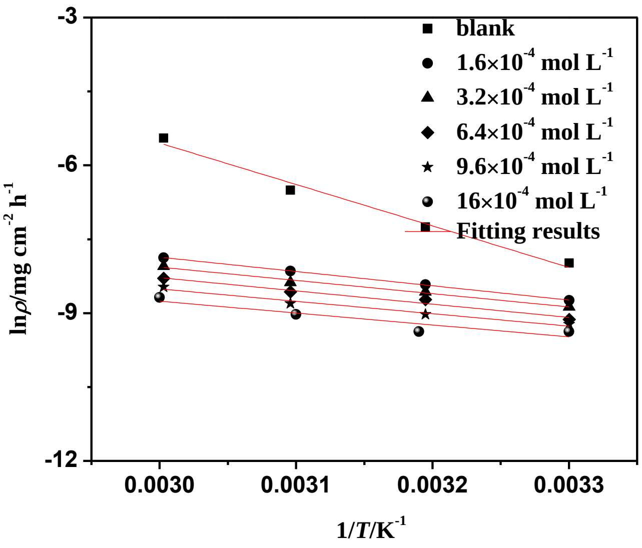

Figure 5. Arrhenius plot for mild steel corrosion in 3 M HCl solution in the absence and presence of different concentrations of BBMB.

The E_a values of mild steel dissolution in 3 M HCl solution without and with different concentration of BBMB can be calculated from the slope of the lnρ versus 1/T plots shown in Fig. 5 and are listed in Table 5. As can be seen, the E_a in the presence of inhibitor is lower than that in the absence of inhibitor. Such low activation energy is the indicative of a strong chemical adsorption between the BBMB molecules and the mild steel surfaces [53-54].

Table 5. Calculated values of activation parameters for mild steel corrosion in 3 M HCl solution in the absence and presence of different concentrations of BBMB.

C	ΔH	ΔS	E_a
/$\times 10^{-4}$ mol L^{-1}	/kJ mol^{-1}	/J mol^{-1} K^{-1}	/kJ mol^{-1}
blank	67.3	-90.9	69.9
1.6	21.4	-246.6	24.1
3.2	19.7	-254.1	22.4
6.4	19.7	-255.7	22.4
9.6	18.3	-261.6	20.9
16	17.5	-266.5	20.1

The enthalpy of activation, ΔH and entropy of activation ΔS were obtained from Eyring transition state equation:

$$\rho = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right) \qquad (10)$$

Where ρ is the corrosion rate (g cm^{-2} h^{-1}), h is the Planck's constant (6.63×10^{-34} Js), N is the Avogadro's number (6.02×10^{23} mol^{-1}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is the absolute temperature (K).

The plots of ln(ρ/T) versus 1/T should give a straight line in uninhibited and inhibited 3 M HCl solution as depicted in Fig. 6. With the slope ($-\Delta H/R$) and the intercept of ($\ln(R/Nh) + \Delta S/R$), the values of ΔH and ΔS can be calculated (given in Table 5). The positive values of ΔH reflect the endothermic nature of the mild steel dissolution process meaning the dissolution of mild steel is difficult in 3 M HCl solution [55]. In comparison with uninhibited solution, the enthalpy value decreases in the presence of BBMB, indicating that the mild steel dissolution reaction was suppressed by the formation of a adsorptive film. Also, the ΔS values are large and negative in 3 M HCl solution in absence and in presence of BBMB and increases negatively with the increasing BBMB concentration, which implies that the activated complex in the rate determining step represents an association process rather than a dissociation step, meaning that an decrease in disorder takes place on going from reactants to the activated complex by the formation of stable adsorption layer of the BBMB molecules on mild steel surface [38, 48, 56].

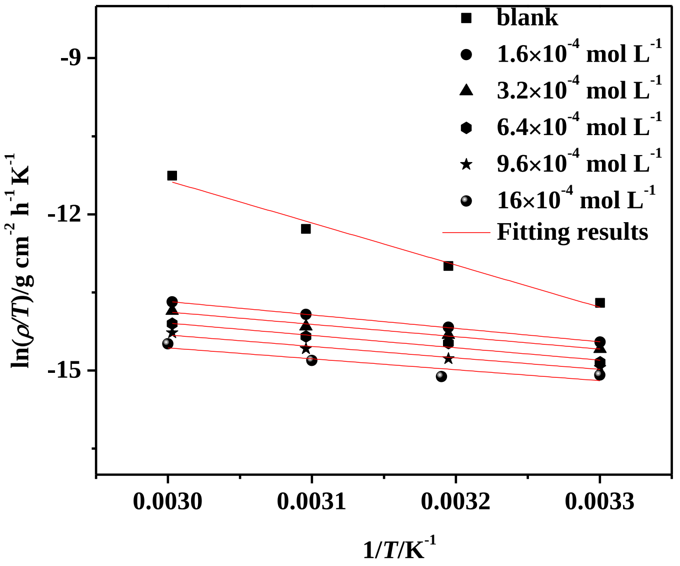

Figure 6. Eyring transition state plot for mild steel corrosion in 3 M HCl solution in the absence and presence of different concentrations of BBMB.

4. CONCLUSIONS

The following results are obtained from the present study:

1. 1, 4- bis (benzimidazolyl) benzene (BBMB) was found to be an excellent inhibitor for mild steel in 3 M HCl solution. The inhibition efficiency increased with the increase in BBMB concentration and temperature, the maximum inhibition efficiency is 96.0% at 333 K and 16×10^{-4} mol L^{-1} (Weight loss results). Weight loss measurements are in reasonable agreement with potentiodynamic polarization curves and EIS methods.

2. BBMB is a mixed type inhibitor by retarding simultaneously both anodic and cathodic reactions.

3. The adsorption of BBMB on the mild steel surface in 3 M HCl solution can be approximated by the Langmuir adsorption isotherm. The adsorption process is a spontaneous and endothermic process accompanied by the negative increase in entropy.

ACKNOWLEDGMENTS
The authors gratefully appreciate the financial support from the National Natural Science Foundation of China (Grant No.: 51101106 and 51131007) and Program for Innovative Research Team by the Ministry of Education (Grant No.: IRT1160).

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