

## Study of Inhibitive Effect of 1,4-bis(benzimidazolyl)benzene on Mild Steel Corrosion in 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> Solutions

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The inhibitive effect of bisbenzimidazole compound 1, 4-bis (benzimidazolyl)benzene (BBMB) on the corrosion of mild steel in 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions was investigated employing weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves methods. The results show that BBMB is a good inhibitor in both acidic media, and exhibits more efficiency in 0.5 M HCl solution than that in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution. The adsorption of BBMB on mild steel surface obeys Langmuir adsorption isotherm in both acids. Potentiodynamic polarization curves reveal that BBMB acts as a mixed-type inhibitor through both reducing the anodic mild steel dissolution reaction and retarding the hydrogen evolution reaction.

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**Keywords:** Mild Steel; Acid Corrosion; Electrochemical Technique; Langmuir

### 1. INTRODUCTION

The use of inhibitors is one of the most practical methods for protecting metal and alloy materials against corrosion, especially in acidic media due to the ease of application [1]. As acidic media, hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) are widely used in industry, some of the important fields of application being acid pickling of steel, chemical cleaning and processing, the removal of undesirable oxide films and corrosion products [2], ore production and oil well acidification. In many industries, mild steel (MS) is the material of choice in the fabrication of reaction vessels, storage tanks etc., which get corroded easily in the presence of acids [3]. Most well-known acid inhibitors are organic heterocyclic compounds containing N, S, P and O atoms [4-7]. The inhibition efficiency of inhibitors increases in the order of: O < N < S < P [8-9]. The efficiency of

these compounds mainly depends on their adsorption abilities on the metal surface with the polar groups acting as the adsorptive centers.

Among various acid organic inhibitors, N-heterocyclic compounds as potential corrosion inhibitors have received a considerable amount of attention. Up to now, many N-heterocyclic compounds with one or several N heteroatoms have been investigated as corrosion inhibitors for mild steel in HCl and H<sub>2</sub>SO<sub>4</sub> solutions [10-23]. It is generally accepted that N-heterocyclic compounds exert their inhibition by adsorption on the metal surface through N heteroatom, as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures. Furthermore, inhibition efficiency of N-heterocyclic organic inhibitor always increases with the increase of the number of aromatic systems and the availability of electronegative atoms in the molecule [24, 25].

Benzimidazole molecule shows two anchoring sites suitable for surface bonding: 1, 3-nitrogen atoms with its lonely sp<sup>2</sup> electron pair and the aromatic rings to facilitate the adsorption of compounds on the metallic surface [26]. Benzimidazole and its derivatives have received widespread research as excellent inhibitors for mild steel and its alloys in acidic solution [15, 27-34] for their characteristics of structure, high inhibition performance, low mammalian toxicity and biodegradation. However, the bis-benzimidazole compounds bearing two end benzimidazole rings separated by carbon chain or other function group as corrosion inhibitor have been rarely reported. So study of bis-benzimidazole compounds as acidic inhibitor of mild steel in acid solution will offer a good reference for new inhibitor development.

In continuation of work on the acid corrosion inhibitors, 1, 4-bis (benzimidazolyl) benzene (BBMB) was used as a corrosion inhibitor for mild steel in 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions. The adsorption of the inhibitor is investigated and some of the thermodynamic adsorption parameters such as the equilibrium constant and standard free energy of adsorption in presence of the inhibitor are calculated. The inhibition performance is evaluated by weight loss measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves measurements. Meanwhile, the comparison of inhibition performance in HCl and H<sub>2</sub>SO<sub>4</sub> solutions are discussed in detail. A probable inhibition mechanism is proposed from the viewpoint of adsorption theory to explain the inhibition performance of the inhibitor for mild steel in both acidic media.

## 2. EXPERIMENTAL

### 2.1. Preparation of electrodes

Mild steel specimens of the composition C=0.15%, Si=0.06%, Mn=0.32%, P=0.05% and the remaining % of Fe were chosen for the present study. The mild steel specimens were cut from a cylindrical rod to a length of 1 cm and inserted to epoxy resin leaving only 0.785 cm<sup>2</sup> of the surface area exposed to electrolyte. Before measurements, the surface of working electrode was mechanically abraded using different grades of emery papers, which ended with the 800 grade. The disc was cleaned

by washing with bidistilled water, thoroughly degreased with acetone, and finally dried with a filter paper, then stored in the vacuum desiccators. For each test, a freshly abraded electrode was used.

## 2.2. Test solutions

The aggressive solutions of 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> was prepared by dilution of AR grade 37% HCl and 98% H<sub>2</sub>SO<sub>4</sub> in distilled water without further purification, respectively. The concentration range of BBMB employed was 0.01–0.20 mM. For each experiment, a freshly prepared solution was used. The test solutions were opened to the atmosphere and the temperature was controlled thermostatically at 298 K using a water thermostat. The experiments were performed under static conditions.

## 2.3. Weight loss measurements

The mild steel sheets of 2.0 cm × 2.0 cm × 0.5 cm were abraded by a series of emery paper (grade 100–400–800) and then washed with distilled water, degreased with acetone, and finally dried with a cold air stream. After weighing accurately by digital balance with sensitivity of ±0.1 mg, the specimens were immersed in beaker containing 250 mL acid solution without and with different concentrations of BBMB using glass hooks and rods for 5 h. After immersion, the specimens were taken out, rinsed thoroughly with distilled water in order to remove the corrosion product, dried with a hot air stream, and reweighed accurately. In order to get good reproducibility, parallel triplicate experiments were performed and the average weight loss value of three parallel mild steel sheets was obtained. The corrosion rate ( $v$ ) was calculated by the following equation:

$$v = \frac{W}{St} \quad (1)$$

Where  $v$  was the corrosion rate in (mg cm<sup>-2</sup> h<sup>-1</sup>),  $W$  is the average weight loss of three parallel mild steel sheets (mg),  $S$  was the total area of one mild steel sheet (cm<sup>2</sup>), and  $t$  was immersion time (h). With the calculated corrosion rate, the inhibition efficiency ( $IE$  %) was obtained as the following equation:

$$IE\% = \frac{v_0 - v}{v_0} \times 100 \quad (2)$$

Where  $v_0$  and  $v$  are the values of corrosion rate without and with different concentration of inhibitor, respectively.

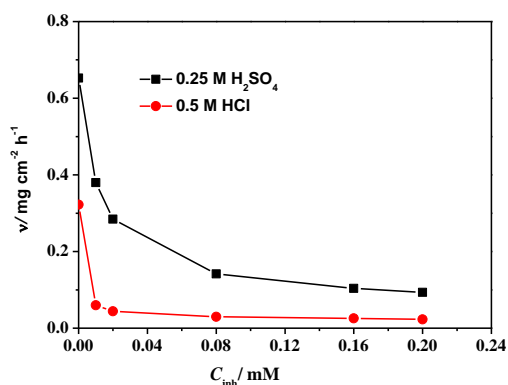
### 2.4. Electrochemical measurements

The PARSTAT 2273 advanced electrochemical system (Princeton Applied Research) was used to record all electrochemical results. Electrochemical experiments were carried out in the conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. To minimize ohmic contribution, the Luggin capillary was close to working electrode (WE). All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 0.5 h to establish a steady open circuit potential ( $E_{OCP}$ ). After measuring the  $E_{OCP}$ , the electrochemical measurements were performed. Potentiodynamic polarization curves were obtained by changing the potential automatically from -150 to +250 mV versus open circuit potential ( $E_{OCP}$ ) with the scan rate of  $0.5 \text{ mV s}^{-1}$ . The electrochemical impedance spectroscopy experiments were conducted in the frequency range of 100 kHz to 0.01 Hz using a 10 mV peak-to-peak voltage excitation at open circuit potential. The potentiodynamic polarization curves and EIS data were analyzed by means of Powersuite and Zsimpwin software, respectively.

## 3. RESULTS AND DISCUSSION

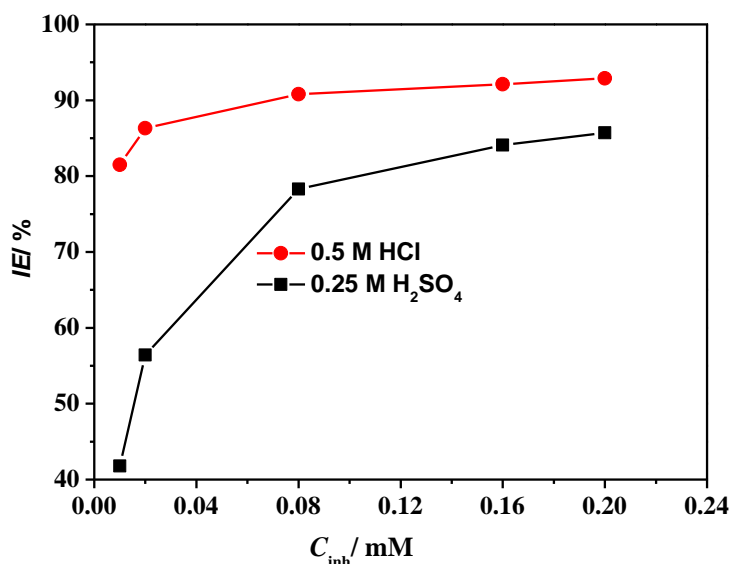
### 3.1. Weight loss study

The weight loss method of monitoring corrosion rate and inhibition efficiency is useful owing to its simple application and good reliability [35-36]. Fig. 1 shows the corrosion rate ( $v$ ) values of mild steel in both 0.5 M HCl and 0.25 M  $\text{H}_2\text{SO}_4$  solutions without and with different concentrations of BBMB at 298 K. In both acidic media, it is obvious that the BBMB effectively inhibits the corrosion rate of mild steel in both HCl and  $\text{H}_2\text{SO}_4$  media. Corrosion rate  $v$  decreases noticeably with an increase in BBMB concentration.



**Figure 1.** Relationship between corrosion rate ( $v$ ) and concentration of BBMB in 0.5 M HCl and 0.25 M  $\text{H}_2\text{SO}_4$  solutions at 298 K.

At the maximum concentration of 0.20 mM BBMB, the corrosion rate values from 0.32 and 0.65  $\text{mg cm}^{-2} \text{h}^{-1}$  are decreased to 0.02 and 0.09  $\text{mg cm}^{-2} \text{h}^{-1}$  in 0.5 M HCl and 0.25 M  $\text{H}_2\text{SO}_4$  solutions, respectively. This behavior is due to the fact that the adsorption amount and coverage of inhibitor on mild steel surface increase with the inhibitor concentration [37]. It should be noted that when the BBMB concentration reaches about 0.16 mM, the corrosion rate value reaches certain data and does not change markedly. At any given inhibitor concentration, the corrosion rate in 0.25 M  $\text{H}_2\text{SO}_4$  solution is comparatively higher than that in 0.5 M HCl solution. This is likely due to the lesser surface coverage in  $\text{H}_2\text{SO}_4$  solution.



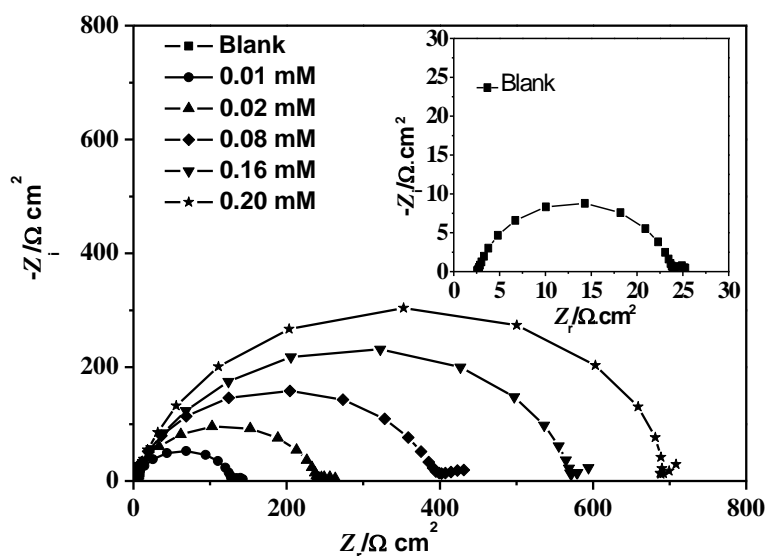
**Figure 2.** Relationship between inhibition efficiency ( $IE\%$ ) obtained from weight loss measurements and concentration of BBMB in 0.5 M HCl and 0.25 M  $\text{H}_2\text{SO}_4$  solutions at 298K.

The variation in inhibition efficiency with concentration of BBMB obtained from weight loss measurements at 298 K is shown in Fig.2. From Fig.2, it is clear to see when the concentration of BBMB is less than 0.16 mM,  $IE\%$  increases sharply with an increase in concentration and exhibits the opposite variation compared to corrosion rate in both 0.5 M HCl and 0.25 M  $\text{H}_2\text{SO}_4$  solutions, especially in 0.25 M  $\text{H}_2\text{SO}_4$  solution, while a further increasing BBMB concentration causes no appreciable change in performance. The increase in inhibition efficiency is due to the increase in the number of BBMB adsorbed on the mild steel surface at higher concentrations, so that the active sites of the metal are protected by BBMB molecules. The maximum  $IE\%$  values are 92.9% (0.5 M HCl) and 85.7% (0.25 M  $\text{H}_2\text{SO}_4$ ) at 0.20 mM concentration which indicates that BBMB is a very good inhibitor for mild steel in both HCl and  $\text{H}_2\text{SO}_4$  solutions.  $IE\%$  values at any inhibitor concentration are higher in 0.5 M HCl solution than that in 0.25 M  $\text{H}_2\text{SO}_4$  solution, especially in low concentration.

3.2. Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of mild steel in 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of different concentrations of BBMB at 298 K was shown in Fig.3 and Fig.4, respectively. In both solutions, the impedance spectra consist of one single depressed semicircle, which indicates that the corrosion of mild steel is mainly controlled by a charge transfer process [38]. Comparing with blank solution, the shape is maintained throughout all tested concentrations, indicating that the presence of the inhibitor did not change the mechanism of mild steel dissolution in both solutions [39]. The characteristic of these capacitive loops in both acid solutions can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface [40]. Furthermore, the diameter of the capacitive loop in the presence of BBMB is bigger than that in the absence of BBMB (blank solution) and increases with the BBMB concentration increasing. This indicates that the impedance of mild steel increases with the BBMB concentration. For analysis of the impedance spectra containing a single capacitive semicircle, the standard Randles circuit is used [41] (in Fig.5) where the circuit is composed of a solution resistance component ( $R_s$ ), a polarisation resistance component ( $R_p$ ) and a capacitance component ( $C_{dl}$ ). Similar figures have been described in literature for the acidic corrosion of iron and steel in the presence and absence of inhibitor molecules [42-43]. Double layer capacitance values ( $C_{dl}$ ) were obtained at maximum frequency ( $f_{max}$ ), at which maginary value reaches a maximum on the Nyquist plot and calculated using the following Eq. (3).

$$C_{dl} = \frac{1}{2\pi f_{max}} \times \frac{1}{R_p} \quad (3)$$

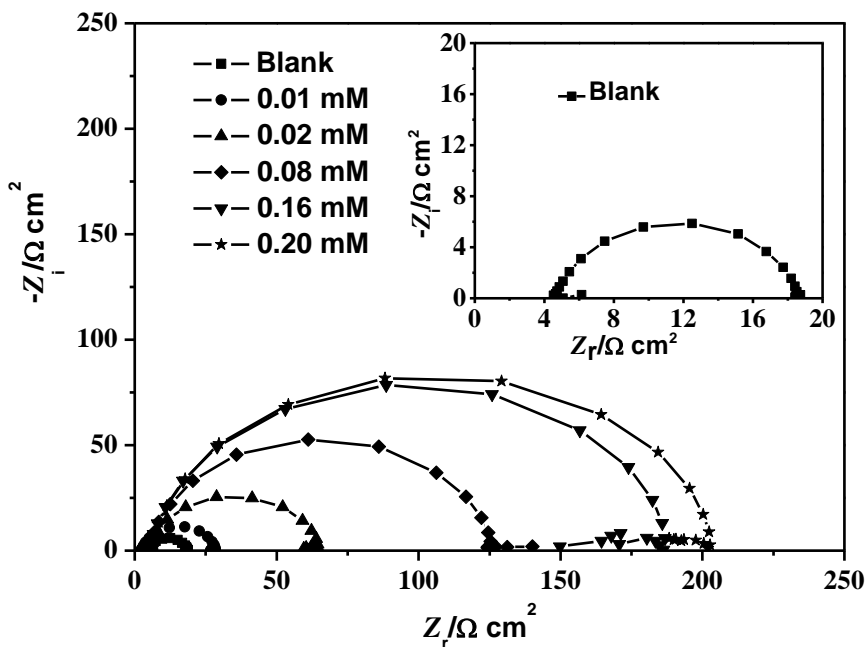


**Figure 3.** Nyquist plots of the corrosion of mild steel in 0.5 M HCl solution without and with addition of different concentrations of BBMB at 298 K.

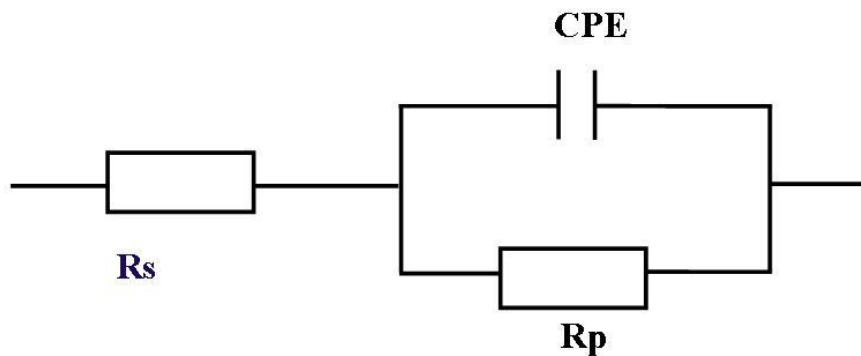
Inhibition efficiency ( $IE\%$ ) is calculated on the basis of the equation:

$$IE\% = \frac{R_{p(inh)} - R_{p(0)}}{R_{p(inh)}} \times 100 \quad (4)$$

where  $R_{p(0)}$  and  $R_{p(inh)}$  are polarisation resistance values of mild steel in both acid solutions without and with addition of various concentration of BBMB, respectively.



**Figure 4.** Nyquist plots of the corrosion of mild steel in 0.25 M  $H_2SO_4$  solution without and with addition of different concentrations of BBMB at 298 K.



**Figure 5.** Equivalent circuit

**Table 1.** EIS parameters for the corrosion of mild steel in 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of different concentration of BBMB at 298 K.

$C_{inh}$	$R_s$	$C_{dl}$	$n$	$R_p$	$IE$	$\theta$ (weight loss)
/ mM	/ $\Omega$ cm <sup>2</sup>	/ $\times 10^{-5}$ F cm <sup>-2</sup>		/ $\Omega$ cm <sup>2</sup>	/%	
0.5 M HCl						
Blank	2.2	35	0.88	19	-	
0.01	2.0	5.2	0.86	128	85.2	0.82
0.02	1.5	2.8	0.87	238	92.0	0.86
0.08	2.1	1.8	0.90	373	94.9	0.91
0.16	1.9	1.3	0.86	525	96.3	0.92
0.20	2.1	1.2	0.87	840	97.7	0.93
0.25 M H <sub>2</sub> SO <sub>4</sub>						
Blank	4.9	56	0.91	14	-	
0.01	4.7	8.8	0.93	25	44.0	0.42
0.02	5.1	3.7	0.91	60	76.7	0.56
0.08	4.7	3.2	0.90	121	88.4	0.78
0.16	5.2	2.1	0.90	182	92.3	0.84
0.20	5.2	1.9	0.89	198	92.9	0.86

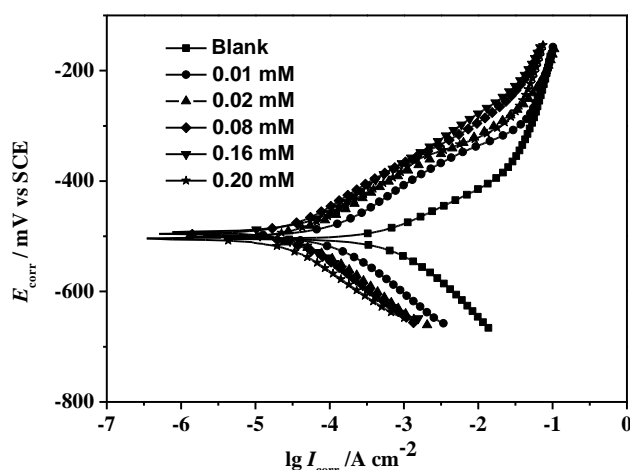
The impedance parameters and inhibition efficiency ( $IE$  %) are given in Table 1. Inspection of Table 1, when the concentration of inhibitor increases, the  $R_p$  and  $IE\%$  increase which indicates that the inhibition of BBMB increases with the increase in the concentration in both media. However, the  $C_{dl}$  values tend to decrease. A decrease in the  $C_{dl}$  values, which can result from a decrease in the local dielectric constant and /or an increase in the thickness of the electrical double layer, suggests that the BBMB molecules function by adsorption at the metal solution/interface [44]. The inhibition efficiency increased with inhibitor concentration, reaching a maximum value at 0.20 mM in both acids. The inhibition efficiency was found to be greater in HCl solution. This may be due to the availability of more sites on the metal surface because of the lesser adsorption of the sulfate ions [45]. These results again confirm that BBMB exhibits good inhibitive performance for mild steel in both acid solutions. The impedance study also gave the same efficiency trend as found in weight loss methods. Inhibition efficiencies obtained from EIS and weight loss are in good reasonably agreement.

### 3.3. Potentiodynamic polarization curves

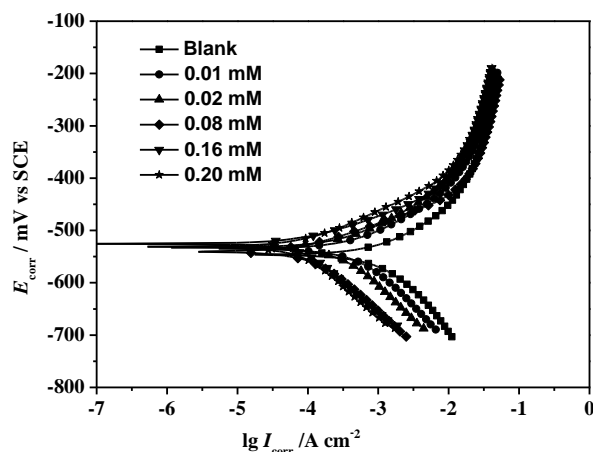
Figs. 6 and 7 show potentiodynamic polarisation plots recorded on mild steel electrode in 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions in absence and presence of different concentrations of BBMB. As



it can be seen, both cathodic and anodic reactions of mild steel electrode corrosion were inhibited with the increase of BBMB concentration in both acids. These results suggest that the addition of BBMB retards anodic dissolution and cathodic hydrogen evolution reaction. For anodic polarization plots, currents densities increase with polarization time increasing at high overpotentials; This is probably caused by the mild steel dissolution and BBMB molecules desorption, above which the BBMB coverage on mild steel surface decreased drastically [46]. At the same BBMB concentration, the anodic polarization curves of mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution with addition of BBMB show similar shape and close current density to that of mild steel in blank solution at lower overpotential, however, in 0.5 M HCl solution, this phenomenon shows at higher overpotential, which indicates the inhibition of BBMB on mild steel corrosion in 0.5 M HCl solution is better than that in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution.



**Figure 6.** Potentiodynamic polarization curves for mild steel in 0.5 M HCl in absence and presence of different concentration of BBMB at 298 K.



**Figure 7.** Potentiodynamic polarization curves for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution in absence and presence of different concentration of BBMB at 298 K.

The electrochemical corrosion parameters including corrosion current densities ( $I_{\text{corr}}$ ), corrosion potential ( $E_{\text{corr}}$ ), cathodic Tafel slope ( $\beta_c$ ), anodic Tafel slope ( $\beta_a$ ) obtained by extrapolation of the Tafel lines and inhibition efficiency ( $IE\%$ ) calculated from equation(5) are presented in Table 2.

$$IE\% = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100 \quad (5)$$

where  $I_{\text{corr}}$  and  $I_{\text{corr(inh)}}$  are corrosion current densities of mild steel in 0.5 M HCl and 0.25 M  $\text{H}_2\text{SO}_4$  solutions without and with BBMB, respectively.

It is seen that the addition of BBMB decreases  $I_{\text{corr}}$  significantly for all the studied concentrations in both acids, and decreases with the increasing BBMB concentration. Correspondingly,  $IE\%$  increases which is due to the increase in the blocked fraction of the electrode surface by adsorption with BBMB concentration increasing. In 0.5 M HCl and 0.25 M  $\text{H}_2\text{SO}_4$  solutions, no definite trend was observed in the shift of  $E_{\text{corr}}$  values in the presence of different concentrations of BBMB, suggesting that BBMB behaves as a mixed-type (anodic/cathodic) inhibitor [47-49] and the inhibition of BBMB on mild steel is caused by geometric blocking effect [50] or the inhibition effect comes from the reduction of the reaction area on mild steel surface. The maximum inhibition efficiency of 98.2% in 0.5 M HCl solution; and 90.2% in 0.25 M  $\text{H}_2\text{SO}_4$  solution was obtained at 0.20 mM. BBMB is a good inhibitor in both acid solutions, and inhibition efficiency in 0.5 M HCl solution is higher than that in 0.25 M  $\text{H}_2\text{SO}_4$  solution at any concentration. The inhibition efficiencies obtained from potentiodynamic polarization curves are in consistence with the results of weight loss and EIS.

**Table 2.** Potentiodynamic polarization parameters for the corrosion of mild steel in 0.5 M HCl and 0.25 M  $\text{H}_2\text{SO}_4$  solutions without and with different concentrations of BBMB at 298 K.

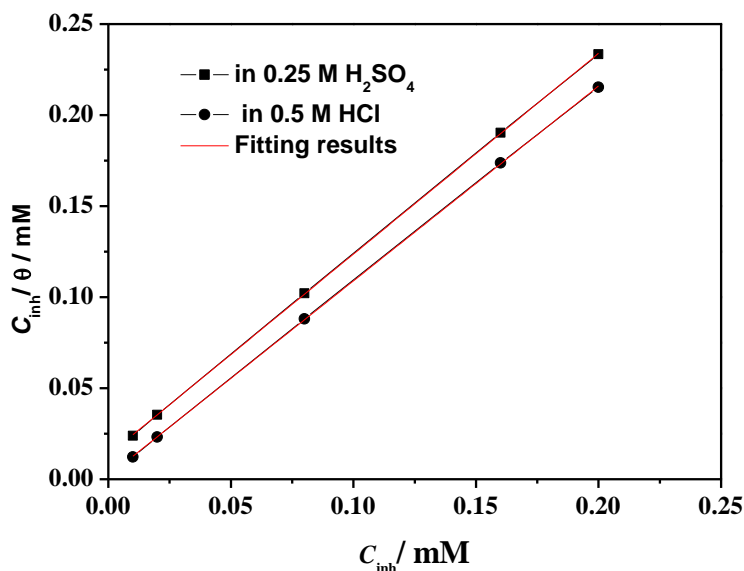
$C_{\text{inh}}$ / mM	$E_{\text{corr}}$ /mV	$I_{\text{corr}}$ / $\times 10^{-5}$ A $\text{cm}^{-2}$	$\beta_a$ /mV	$\beta_c$ /mV	$IE$ %
0.5 M HCl					
Blank	-504	71	84	121	-
0.01	-500	11	93	108	84.5
0.02	-501	5.2	90	106	92.7
0.08	-495	3.3	89	100	95.3
0.16	-494	1.9	90	108	97.4
0.20	-505	1.3	73	86	98.2
0.25 M $\text{H}_2\text{SO}_4$					
Blank	-531	99	103	141	-
0.01	-552	49	117	144	50.9
0.02	-532	38	92	156	61.2
0.08	-541	13	62	128	87.2
0.16	-526	11	65	144	88.9
0.20	-531	9.7	69	136	90.2

3.4 Adsorption isotherm and thermodynamics calculations

The inhibition action of an inhibitor in aggressive acid media is assumed to be its adsorption at the metal/solution interface. The interactions of BBMB and the mild steel surface can be examined by the adsorption isotherm. The degree of surface coverage values ( $\theta$ ) for various concentrations of BBMB in both solutions have been estimated from the weight loss measurements (Table 1). Attempts were made to fit experimental data to various isotherms including Langmuir, Frumkin, Temkin, Freundlich, Bockris-Swinkels isotherms. Suitable adsorption isotherm obtained was Langmuir isotherm. This isotherm can be represented as:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (6)$$

where  $C_{inh}$  is the concentration of inhibitor,  $K_{ads}$  is the adsorptive equilibrium constant.



**Figure 8.** Langmuir isotherm adsorption mode of BBMB on the mild steel surface in 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions at 298 K from weight loss measurement and fitting results.

The linear relationships of  $C_{inh}/\theta$  versus  $C_{inh}$  were depicted in Fig. 8. The linear regression parameter  $r$ , slope, the adsorptive equilibrium constant  $K_{ads}$  ( $L\ mol^{-1}$ ) calculated from the Langmuir adsorption are listed in Table 3. Both linear correlation coefficient ( $r$ ) and slope are very close to 1, clearly indicating that the adsorption of BBMB on mild steel surface obeys the Langmuir adsorption

isotherm in both acid solutions. The inhibition tendency of BBMB is due to the adsorption of BBMB molecules on the metal surface [51]. The relatively high values of the adsorption equilibrium constant reflect the high adsorption ability of these molecules on mild steel surface. Table 3 also shows that  $K_{\text{ads}}$  of in 0.5 M HCl solution is higher than that in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution, which indicates that BBMB exhibits a stronger tendency to adsorb on mild steel surface in 0.5 M HCl solution. The value of  $K_{\text{ads}}$  is related to the standard free energy of adsorption,  $\Delta G_{\text{ads}}^0$ , by the following Equation. (7).

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5K_{\text{ads}}) \quad (7)$$

where  $R$  (8.314 J K<sup>-1</sup> mol<sup>-1</sup>) is the universal gas constant and  $T$  (K) is the absolute temperature. The value of 55.5 is the molar concentration of water in solution expressed in mol L<sup>-1</sup>. The calculated  $\Delta G_{\text{ads}}^0$  values are also presented in Table 3.

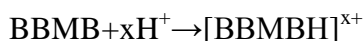
**Table 3.** Thermodynamic parameters for BBMB as corrosion inhibitor of mild steel in 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions.

solution	$K_{\text{ads}}$	$-\Delta_r G_{\text{ads}}^0$	slope	intercept	correlation coefficient ( $r$ )
	/ L mol <sup>-1</sup>	/kJ mol <sup>-1</sup>		mM	
0.25 M H <sub>2</sub> SO <sub>4</sub>	$7.47 \times 10^4$	37.8	1.07016	0.01338	0.99996
0.5 M HCl	$5.21 \times 10^5$	42.6	1.10275	0.00192	0.99995

The negative sign of  $\Delta G_{\text{ads}}^0$  indicates that the BBMB molecules are spontaneously adsorbed onto the metal surface [52]. Generally speaking, the magnitude of  $\Delta G_{\text{ads}}^0$  around 20 kJ mol<sup>-1</sup> or less is assumed for electrostatic interactions exist between the charged inhibitor molecules and the charged metal surface (physical adsorption) [53]. While those around 40 kJ mol<sup>-1</sup> or more indicate electron transferring from organic species to the metal surface, to form a coordinate type of metal bond (chemisorption) [54]. Considering the present study, the calculated values of  $\Delta G_{\text{ads}}^0$  are found to be around -40 kJ mol<sup>-1</sup>; means that the adsorption mechanism of BBMB on mild steel surface is mainly the chemisorption in both solutions. It is generally accepted that chemisorption is always accompanied by physisorption [55]. Therefore, the adsorption of BBMB on mild steel surface involves both chemisorption and physisorption and physical adsorption is preceding stage of chemisorption of inhibitor on metal surface.

Two adsorption modes can be considered BBMB molecule are adsorbed on the mild steel surface due to the free electron pairs on N atoms as well as  $\pi$ -electrons of the aromatic rings in both

acidic media, Owing to neutral N atoms in BBMB, BBMB could be protonated in the acid solution as following:



In both HCl and H<sub>2</sub>SO<sub>4</sub> solutions, the mild steel surface carries positive charge owing to iron dissolution. The adsorption of cationic species would be affected by the surface concentration of anions, the neutral species being adsorbed when possible on free surface sites. Thus it is difficult for the protonated BBMB to approach the positively charged mild steel surface due to the electrostatic repulsions. Therefore, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions should be first adsorbed onto the positively charged metal surface due to a smaller degree of hydration, they created an excess negative charge towards the solution and favor more adsorption of cations. The positively charged BBMB molecules adsorb through electrostatic interactions and form a protective layer on mild steel surface. It is generally accepted that Cl<sup>-</sup> ions have stronger tendency to adsorb SO<sub>4</sub><sup>2-</sup> ions [46]. Moreover, the lesser interference by sulfate ions with the adsorbed protonated cations may lead to lower adsorption and inhibition performance of mild steel corrosion in H<sub>2</sub>SO<sub>4</sub> solution than that in HCl solution (in Fig.2, Table 1 and Table 2). Besides physisorption, BBMB may be adsorbed on the metal surface via strong chemisorption, involving the coordinate bonds that may be formed between the lone electrons pairs of the unprotonated N atoms and  $\pi$ -electrons of aromatic rings and vacant d-orbitals of Fe atoms which enhanced the combination intensity between the BBMB molecules and mild steel electrode surface.

#### 4. CONCLUSIONS

1, 4-bis (benzimidazolyl)-benzene (BBMB) were tested as a possible corrosion inhibitor for mild steel in both 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions by weight loss and electrochemical techniques. The conclusions were drawn as follows:

(1) The compound BBMB has been proven to be an efficient inhibitor for the corrosion of mild steel in both acid solutions. The inhibition efficiencies of BBMB for mild steel tend to increase and corrosion rates of mild steel tend to decrease with increasing BBMB concentration in both acidic media. The inhibition performance in 0.5 M HCl solution is higher than that in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution at any BBMB concentration especially at lower concentration, and the maximum *IE*% values are 92.9% (0.5 M HCl) and 85.7% (0.25 M H<sub>2</sub>SO<sub>4</sub>) at 0.20 mM (in weight loss measurements).

(2) The inhibition efficiencies obtained from weight loss are in good agreement with potentiodynamic polarisation curves and EIS methods.

(3) The potentiodynamic polarisation curves demonstrated that BBMB acts as a mixed-type inhibitor by both reducing anodic mild steel dissolution reaction and inhibiting the cathodic hydrogen evolution reaction.

(4) The values of  $K_{\text{ads}}$  and  $\Delta G_{\text{ads}}^0$  suggest spontaneous and strong interaction of BBMB molecules with mild steel surface and adsorption phenomenon involves physisorption and chemisorption that follows the Langmuir adsorption isotherm in both 0.5 M HCl and 0.25 M H<sub>2</sub>SO<sub>4</sub> solutions. The excellent inhibitive property of BBMB may be ascribed to the compact BBMB adsorptive film preventing mild steel from corrosion in both media.

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