

## Synergistic Inhibition Between Bisbenzimidazole Derivative and Chloride Ion on Mild Steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> Solution

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The inhibition of single 1, 4-bis (benzimidazolyl) butane (BBB) and the mixture of BBB and 0.1 M NaCl on the corrosion of mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution was studied using weight loss and electrochemical methods. Results obtained revealed that BBB and BBB-NaCl mixture suppressed the mild steel corrosion effectively in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution and inhibition efficiency increases with the increasing BBB concentration. At any concentration, together with chloride ion, BBB is more effective corrosion inhibitor compared to single BBB for mild steel corrosion. Potentiodynamic polarization curves studies showed that single BBB and BBB-NaCl mixture are both mixed inhibitors for the corrosion of mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution. The adsorption of BBB and BBB-NaCl mixture on mild steel surface obeys Langmuir adsorption isotherm. The adsorption of BBB-NaCl mixture is stronger than that of BBB. Good synergism exists between NaCl and BBB. There is a good agreement between weight loss and electrochemical results.

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**Keywords:** Corrosion inhibition; Mild steel; Sulfuric acid; Synergistic inhibition

### 1. INTRODUCTION

Mild steel as an important construction material is extensively used in all kinds of industry and corrosion of mild steel known to occur especially in acid environment such as cleaning, pickling, oil well acidification and descaling processes [1-5]. It is a major task to control the mild steel corrosion for both corrosion scientist and material technologist. Several methods are employed to prevent mild steel from corrosion but addition of inhibitors has been known to be the most effective method for its practical application [6-9]. A large number of studies about various types of organic inhibitors have been previously reported [10-32]. Organic molecules can form a barrier through adsorption on the metal surface to reduce the corrosion of metal in acidic solution [33, 34]. So most of efficient

inhibitors are organic compounds in their structures containing heteroatoms (such as, N, S, P and O) donating lone pair electrons, unsaturated bonds (such as double bonds, or triple bonds), and plane conjugated systems including all kinds of aromatic cycles [35-46]. Furthermore, organic inhibitor adsorption on metal surface is influenced by organic inhibitor nature, surface charges on the metal, the type of aggressive solution, and the interaction of inhibitor with the metal surface. In sulphuric acid solution, the metal surface due to its dissolution and organic inhibitor which is protonated carries positive charge [47]. The protonated organic inhibitor would be less adsorbed onto the metal surface leading to lower inhibition efficiencies due to the electrostatic interaction of positive charge. However, the adding halide ions in acid solution has been known to increase the adsorption coverage of organic inhibitor on metal surface and inhibition efficiency as a result [48, 49]. This phenomenon can be considered as a good method to get better inhibition performance, lower amount of usage of the inhibitor and lower cost. In general, in acid media, halide ions are proven to form intermediates on a metal surface, consequently, reduce or accelerate metal dissolution by replacing  $\text{OH}^-$  ions already adsorbed on metal surface during the anodic process. The inhibitive performance of different halide ions has been investigated as following in the sequency:  $\text{I}^- \gg \text{Br}^- > \text{Cl}^-$  [30, 50]. Extensive studies have reported the synergistic inhibition effects between inorganic halide ions and organic inhibitors for the mild steel corrosion in acid solution [51-60].

We have already reported BBB as the corrosion inhibitor of mild steel in 0.5 M HCl solution [61]. In this paper, we aimed to explore the influence of chloride ion on the corrosion inhibition property of BBB on mild steel in 0.25 M  $\text{H}_2\text{SO}_4$  solution and discuss the synergistic inhibition mechanism.

## 2. EXPERIMENTAL METHODS

### 2.1. Materials

The experiments were carried out with mild steel specimens with the composition as follows: C, 0.15%; P, 0.05%; Mn, 0.32%; S, 0.01%; Si, 0.06%; Fe, remainder.

### 2.2. Solutions

All the aggressive media were prepared by dilution of AR grade of  $\text{H}_2\text{SO}_4$  without further purification. 0.005-0.5 mM BBB without and with addition of 0.1 M NaCl in 0.25 M  $\text{H}_2\text{SO}_4$  solution were prepared for tests.

### 2.3. Weight loss measurements

Before experiment, the mild steel sheets of 20 mm × 20 mm × 5 mm were mechanically abraded with 100, 200, 400, 600, 800 and 1000 grades of emery paper. Then, the mild steel sheets

were washed with bidistilled water and alcohol respectively, and finally dried. After weighing accurately, the mild steel sheets were immersed in flask, containing 250 mL 0.25 M H<sub>2</sub>SO<sub>4</sub> solution with and without addition of different concentrations of BBB in the presence and absence of 0.1 M NaCl. All the experiments were open to air. The temperature for all tests was kept at 25 ± 1 °C. After immersion for 6 h, the mild steel sheets were taken out, washed with bidistilled water and acetone several times, then dried and reweighed accurately. All the tests were repeated three times in each experiment. The corrosion rates ( $r_{\text{corr}}$ ) of mild steels and the inhibition efficiency ( $IE\%$ ) were calculated by the relations:

$$r_{\text{corr}} = \frac{m_1 - m_2}{st} \quad (1)$$

$$IE(\%) = \left(1 - \frac{r_{\text{corr}}}{r'_{\text{corr}}}\right) \times 100 \quad (2)$$

where  $m_1$  (mg) is the mass of the specimen before immersion,  $m_2$  (mg) the mass of the specimen after immersion,  $s$  (cm<sup>2</sup>) is the total area of the specimen,  $t$  (h) is immersion time, respectively.  $r_{\text{corr}}$  and  $r'_{\text{corr}}$  are the corrosion rates of mild steel with and without the addition of inhibitor in acid solution, respectively.

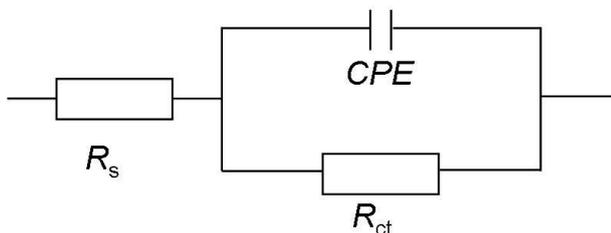
#### 2.4. Electrochemical measurements

Experiments were conducted using a conventional three electrode cell system. The working electrode was mild steel sample exposing 0.785 cm<sup>2</sup> area to corrosive media and the rest being covered with polyester, a rectangular platinum foil of 2 cm<sup>2</sup> and saturated calomel electrode were used as auxiliary electrode and reference electrode, respectively. Prior to each experiment, the working electrode was grinded with 100-1000 grades of sand papers, washed with bidistilled water several times, degreased with alcohol and dried. Investigations have been made with BBB in the concentration range of 0.005–0.5 mM in the presence and absence of 0.1 M NaCl. All electrochemical measurements were carried out on PARSTAT 2273 Potentiostat/Galvanostat (Princeton Applied Research) kept at 25°C ± 1 under static condition. The potentiodynamic polarization curves was performed from a cathodic potential of -150 mV to an anodic potential of + 250 mV with respect to the corrosion potential at a scan rate of 0.5 mV/s and were extrapolated to corrosion potential (OCP) to obtain the corrosion current densities ( $I_{\text{corr}}$ ). The inhibition efficiency ( $IE\%$ ) was evaluated from the obtained  $I_{\text{corr}}$  values using the formula:

$$IE(\%) = \left(1 - \frac{I_{\text{corr}}}{I'_{\text{corr}}}\right) \times 100 \quad (3)$$

where  $I_{\text{corr}}$  and  $I_{\text{corr}}$  ( $\text{mA cm}^{-2}$ ) are the corrosion current density values without and with the addition of various inhibitor.

Electrochemical impedance spectroscopy (EIS) was conducted at signal of 10 mV amplitude and a frequency spectrum from 100 kHz to 0.01 Hz. The Nyquist plots of the impedance data were fitted with Zview software. The impedance data were analyzed by the equivalent circuit shown in Fig.1.



**Figure 1.** The equivalent circuit.

Where  $R_s$  ( $\Omega \text{ cm}^2$ ) is the solution resistance,  $R_{\text{ct}}$  ( $\Omega \text{ cm}^2$ ) is the charge transfer resistance and  $CPE$  is the constant phase element. The charge transfer resistance ( $R_{\text{ct}}$ ) is obtained from the diameter of the semicircle in Nyquist plots. The inhibition efficiency ( $IE\%$ ) was calculated by the equation:

$$IE(\%) = \left(1 - \frac{R_{\text{ct}}}{R_{\text{ct}}}\right) \times 100 \quad (4)$$

where  $R_{\text{ct}}$  and  $R'_{\text{ct}}$  are the charge transfer resistance values without and with addition of inhibitors.

### 3. RESULTS AND DISCUSSION

#### 3.1. Weight loss measurements

Table 1 shows corrosion rates, inhibition efficiencies of single 0.1 M NaCl, single BBB and the mixture of BBB and 0.1 M NaCl determined by the weight loss measurements on mild steel in 0.25 M  $\text{H}_2\text{SO}_4$  solution, respectively. 0.1 M NaCl shows some inhibition for mild steel in 0.25 M  $\text{H}_2\text{SO}_4$  solution, however, the inhibition efficiency is relatively low (37.2%). It is observed that the corrosion rates of mild steel with addition of single BBB, the mixture of BBB and 0.1 M NaCl drastically decrease with increasing the concentration of BBB and inhibition efficiencies increase as a whole. However, at BBB concentrations above 0.04 mM, in the presence of 0.1 M NaCl increasing BBB

concentration does not affect corrosion rate and inhibition efficiency obviously. Single BBB and the mixture of BBB-NaCl exhibit excellent inhibition effect on mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution. At any BBB concentration, the complex of BBB and 0.1 M NaCl has a higher inhibition efficiency (*IE*%), that is to say, the addition of NaCl further increases the inhibition efficiency values, especially obvious at lower BBB concentration. For example, at 0.005 mM BBB is has 35% *IE*, single 0.1 M NaCl has 37% *IE*, while the mixture 0.005 mM BBB and 0.1 M NaCl has 63% *IE*. The result means that there is strong synergistic inhibition between BBB and NaCl to prevent the mild steel from H<sub>2</sub>SO<sub>4</sub> corrosion.

**Table 1.** The corrosion rate, inhibition efficiency and coverage of single 0.1 M NaCl, single BBB, the mixture of BBB and 0.1 M NaCl for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution obtained from the weight loss measurements at 25°C ± 1.

<i>C</i> <sub>inh</sub> / mM	<i>r</i> <sub>corr</sub> / mg h <sup>-1</sup> cm <sup>-2</sup>	<i>IE</i> / %	<i>θ</i>
blank	1.7342	-	-
0.005	1.1235	35.2	0.35
0.01	0.8826	49.1	0.49
0.04	0.6370	63.3	0.63
0.16	0.3642	73.3	0.79
0.50	0.2948	80.2	0.83
0.1 M NaCl	1.0892	37.2	0.37
0.005	0.6002	65.4	0.65
0.01	0.2567	85.2	0.85
0.04	0.1936	88.9	0.89
0.16	0.1321	92.3	0.92
0.50	0.1063	93.9	0.94

### 3.2. Adsorption isotherm

To understand the mechanism of BBB corrosion inhibition on mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution, the adsorption behavior of BBB on mild steel surface must be illustrated. The character of adsorption of single BBB and BBB in combination with 0.1 M NaCl was elucidated from the degree of surface coverage (*θ*) values (*θ* equal to *IE*% × 100)[62, 63] listed in Table 1 corresponding to different concentrations of BBB obtained from the weight loss results. The values of coverage for single BBB and BBB-NaCl mixture on mild steel surface have been attempted to fit with various adsorption isotherms including the Langmuir adsorption isotherm, Temkin adsorption isotherm and Freundlich adsorption isotherm. By far, the Langmuir adsorption isotherm is the best fits. The Langmuir adsorption isotherm is expressed by

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

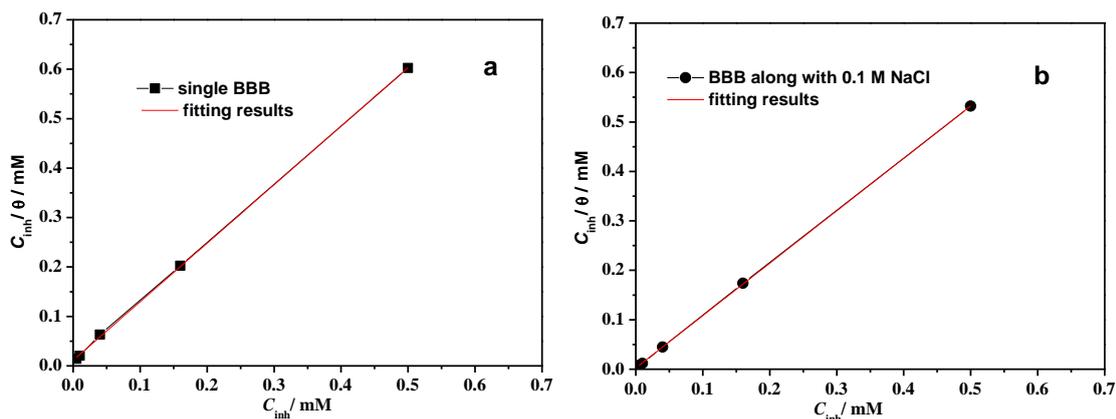
Where  $\theta$  is the degree of surface coverage,  $C$  (mM) is the inhibitor BBB concentration and  $K$  ( $\text{L mol}^{-1}$ ) is the adsorption equilibrium constant corresponding to the following relation:

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{\text{ads}}}{RT}\right) \quad (6)$$

The linear regression between  $C/\theta$  and  $C$  was obtained by origin 8.0 software,  $K$  and  $\Delta G_{\text{ads}}$  can be calculated according to above two equations (equation (5) and (6)). Fig. 2 shows the plot of surface coverage ( $\theta$ ) as a function of logarithm of BBB concentration (Fig. 2a) and BBB-NaCl mixture (Fig. 2b). The adsorption parameters calculated from Langmuir adsorption isotherm are presented in Table 2 for mild steel corrosion in 0.25 M  $\text{H}_2\text{SO}_4$  solution in the presence of single BBB and BBB-NaCl mixture. It is obvious that the correlation coefficients and the slopes of straight lines  $C/\theta$  versus  $C$  of BBB and BBB-NaCl mixture all approach 1. This illustrates that the adsorption of BBB and BBB-NaCl mixture on mild steel surface conforms to Langmuir adsorption isotherm. The negative adsorption free energy  $\Delta G_{\text{ads}}$  mean that the adsorption of BBB and BBB-NaCl mixture on mild steel surface is a spontaneous process. As it is known, for values of  $\Delta G_{\text{ads}}$  up to  $-20 \text{ kJ mol}^{-1}$ , the adsorption type was considered as physical adsorption, where the inhibition occurs due to the electrostatic attractions between the charged metal surface and the charged inhibitor molecules. For  $\Delta G_{\text{ads}}$  values of  $-40 \text{ kJ mol}^{-1}$  or more negative were regarded as chemical adsorption, which include the charge sharing or electron transfer from the inhibitor molecules to the metal surface, thus to form a coordinate bond. Table 2 showed that the calculated values of  $\Delta G_{\text{ads}}$  were  $-38.2 \text{ kJ mol}^{-1}$  for single BBB and  $-42.0 \text{ kJ mol}^{-1}$  for BBB-NaCl mixture, respectively. This suggested that BBB and BBB-NaCl mixture were adsorbed chemically onto the mild steel surface [64-65]. It is generally accepted that  $K$  denotes the adsorption strength between the inhibitor and metal surface. Larger values of  $K$  indicate more efficient adsorption and hence higher inhibition efficiency [66]. Larger  $K$  value for BBB-NaCl mixture than that for single BBB indicates that the adsorption of BBB-NaCl mixture is stronger than that of single BBB on mild steel surface which is due to good synergistic effect between BBB and NaCl.

**Table 2.** Parameters obtained from Langmuir isotherm plot at  $25^\circ\text{C} \pm 1$  for mild steel in 0.25 M  $\text{H}_2\text{SO}_4$  solution with BBB and BBB-NaCl mixture.

system	$K_{\text{ads}}$	$-\Delta G_{\text{ads}}$	slope	intercept	correlation coefficient ( $r$ )
	/ $\text{L mol}^{-1}$	/ $\text{kJ mol}^{-1}$		/ mM	
BBB	$8.8 \times 10^4$	38.2	1.18	0.01133	0.99976
BBB+0.1 M NaCl	$4.1 \times 10^5$	42.0	1.06	0.00246	0.99996



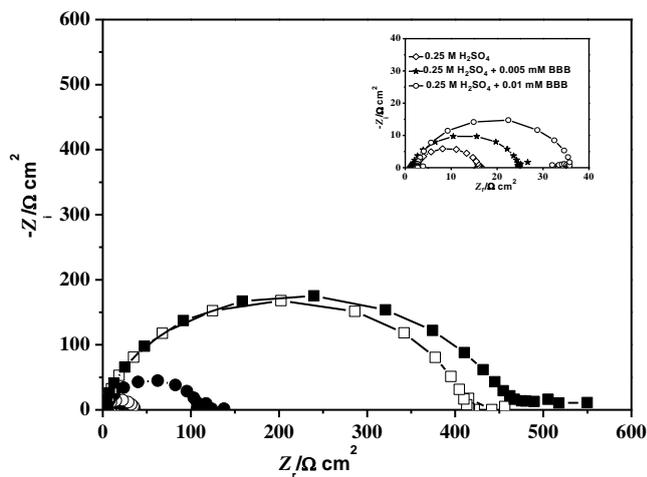
**Figure 2.** Relationship between  $C/\theta$  and  $C$  of BBB (a) and BBB-NaCl mixture (b) for mild steel in 0.25 M  $\text{H}_2\text{SO}_4$  solution at  $25^\circ\text{C} \pm 1$ .

### 3.3. Electrochemical Impedance Spectroscopy (EIS)

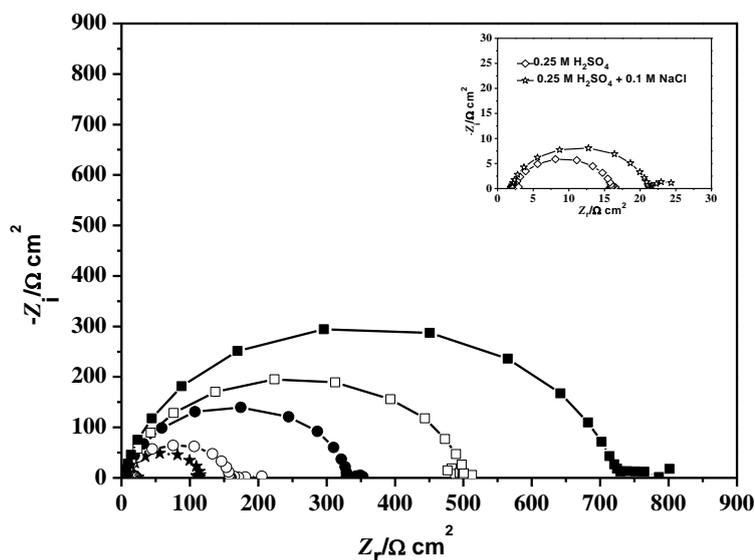
Fig. 3 shows the Nyquist plots of mild steel at the corrosion potentials in 0.25 M  $\text{H}_2\text{SO}_4$  solution with addition of different concentration of BBB. The characteristic of a single semicircle shows the existence of single charge transfer process during mild steel dissolution which is unaffected by BBB molecules. The slightly depressed capacitive loop which has the center below the x-axis is the representation for solid electrodes and the frequency dispersion has been ascribed to the inhomogenities of the solid electrode [67, 68]. Fig.1 was used to model mild steel surface and solution interface. The solution resistance ( $R_s$ ), the charge transfer resistance ( $R_{ct}$ ), the interfacial double layer capacitance ( $C_{dl}$ ) values derived from these plots and the calculated inhibition efficiency ( $IE\%$ ) according to equation (3) are given in Table 3. It is clear that the addition of BBB increases the value of  $R_{ct}$  from the value of  $14 \Omega \text{ cm}^2$  (blank) to  $442 \Omega \text{ cm}^2$  (0.5 mM BBB) and this in turn leads to an increase in the inhibition efficiency from 41.7% to 96.8% (0.005-0.5 mM BBB). On the other hand, the addition of BBB lowers the  $C_{dl}$  value from 191 to  $21 \mu\text{F cm}^{-2}$ . Decrease in  $C_{dl}$ , which is due to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the BBB function by adsorption at the mild steel–solution interface [69].

Fig. 4 shows the impedance behaviour of mild steel in 0.25 M  $\text{H}_2\text{SO}_4$  solution containing single 0.1 M NaCl and 0.1 M NaCl along with various concentrations of BBB. For single 0.1 M NaCl and BBB-NaCl mixture, similar impedance plots have been observed. The impedance plots also are fitted by the equivalent circuit shown in Fig.1. The charge transfer resistance, the double layer capacitance with the constant phase element methodology obtained from the plots and  $IE\%$  are presented in Table 3. The increase of charge transfer resistance value from 14 to  $707 \Omega \text{ cm}^2$  resulting in 98.0% of inhibition efficiency for 0.5 mM BBB has expressed the synergistic action of 0.1 M NaCl along with

BBB on mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution. At the same BBB concentration, the  $R_{ct}$  for single BBB is lower than that for the mixture of BBB and 0.1 M NaCl, the inhibition efficiency shows the same trend which can be explained that there is synergism between BBB and NaCl.



**Figure 3.** Nyquist plots for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution in presence of various concentrations of BBB at 25 °C ± 1: blank (-◇-); 0.005 mM BBB (-★-); 0.01 mM BBB (-○-); 0.04 mM BBB (-●-); 0.16 mM BBB(-□-); 0.50 mM BBB (-■-).



**Figure 4.** Nyquist plots for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution with the addition of different concentrations of BBB without and with addition of 0.1 M NaCl at 25 °C ± 1: blank H<sub>2</sub>SO<sub>4</sub>(-◇-); 0.1 M NaCl(-☆-); 0.1 M NaCl + 0.005 mM BBB (-★-); 0.1 M NaCl + 0.01 mM BBB (-○-); 0.1 M NaCl + 0.04 mM BBB (-●-); 0.1 M NaCl + 0.16 mM BBB (-□-); 0.1 M NaCl + 0.50 mM BBB (-■-).

**Table 3.** Electrochemical impedance parameters and inhibition efficiency for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution with BBB, 0.1 M NaCl, BBB-NaCl mixture at 25 °C ± 1.

$C_{inh}$	$R_s$	$C_{dl}$	n	$R_{ct}$	$IE$
/ mM	/ $\Omega\text{ cm}^2$	/ $\mu\text{F cm}^{-2}$		/ $\Omega\text{ cm}^2$	/ %
blank	4.4	191	0.92	14	-
0.005	4.2	163	0.87	24	41.7
0.01	4.7	78	0.93	33	57.6
0.04	4.4	37	0.88	107	86.9
0.16	4.4	27	0.90	406	96.6
0.50	4.3	21	0.90	442	96.8
0.1 M NaCl	3.9	161	0.92	19	26.3
0.005	5.5	70	0.89	113	87.6
0.01	4.9	48	0.90	154	90.9
0.04	4.8	32	0.90	327	95.7
0.16	4.6	18	0.88	491	97.1
0.50	4.8	17	0.91	707	98.0

### 3.4. Potentiodynamic polarization curves

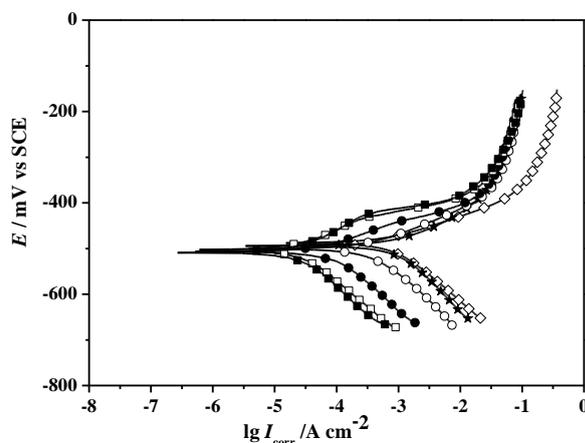
Potentiodynamic polarization curves for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution in the absence and the presence of various concentrations of single BBB at 25°C ± 1 are shown in Fig. 5, it is seen obviously that addition of single BBB shows no change in the corrosion potential of mild steel but only lowers both the anodic and cathodic current densities, which indicates that BBB inhibits both cathodic reaction of mild steel and anodic hydrogen reduction in 0.25 M H<sub>2</sub>SO<sub>4</sub> simultaneously, and it can be obtained a better inhibition performance at a higher BBB concentration. Potentiodynamic polarization curves for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution with various concentrations of BBB without and with addition of 0.1 M NaCl at 25°C ± 1 are depicted in Fig. 6. The anodic and cathodic reaction is inhibited by the presence of single 0.1 M NaCl. As for the mixture of BBB and NaCl, both anodic and cathodic reactions are greatly inhibited by the mixture. It clearly indicates that the mild steel corrosion is dramatically inhibited by the presence of a small quantity of mixture compared to single BBB. The electrochemical parameters obtained by extrapolation were all listed in Table 4. Where,  $E_{corr}$ ,  $I_{corr}$ ,  $\beta_a$ ,  $\beta_c$  and  $IE\%$  were the corrosion potential, corrosion current density, anode Tafel slope, cathode Tafel slope and inhibition efficiency, respectively. From Table 4, with increasing BBB concentration without and with addition of 0.1 M NaCl, the current density decreases, inhibition efficiency increases, the corrosion potential do not be shifted to anodic or cathodic direction, meaning that single BBB and the complex behave as mixed-type inhibitors. At the same BBB concentration, the current density of single BBB is higher than that of the complex of BBB and 0.1 M NaCl, however, the inhibition

efficiency shows opposite trend. The results also indicate that there is a strong synergistic inhibition between BBB and NaCl for mild steel corrosion in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution [70].

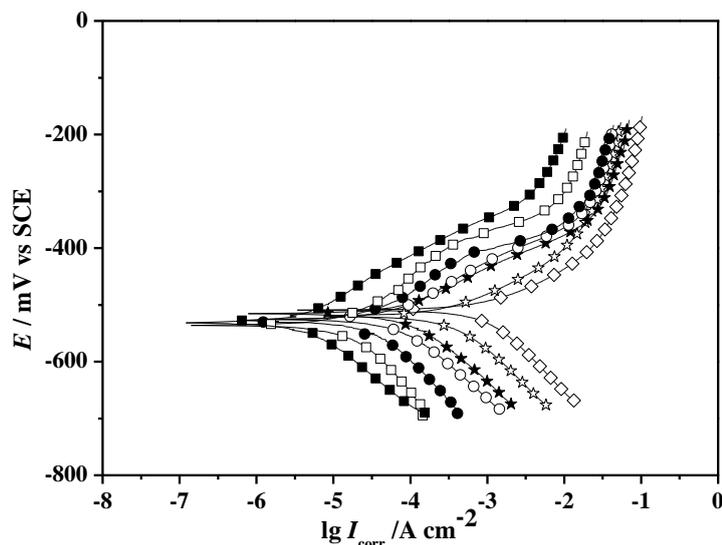
**Table 4.** Electrochemical parameters and inhibition efficiency (*IE*%) for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution with single BBB, 0.1 M NaCl, BBB-NaCl mixture at 25 °C ± 1.

$C_{inh}$ / mM	$E_{corr}$ / mV	$I_{corr}$ / mA cm <sup>-2</sup>	$\beta_a$ / mV	$\beta_c$ / mV	<i>IE</i> / %
blank	-509	1.5	98	194	-
0.005	-498	0.70	63	124	53.3
0.01	-501	0.58	71	134	61.4
0.04	-507	0.069	54	109	95.4
0.16	-503	0.035	67	91	97.7
0.50	-509	0.021	63	110	98.6
0.1 M NaCl	-535	0.85	90	147	43.3
0.005	-515	0.069	88	107	95.4
0.01	-525	0.045	82	115	97.0
0.04	-528	0.030	88	135	98.0
0.16	-536	0.019	104	113	98.8
0.50	-531	0.015	90	110	99.0

It is clearly seen that, there is a good agreement between weigh loss measurement and electrochemical technique, where the two different methods gave the same trend of corrosion inhibition of single BBB and the complex of BBB along with 0.1 M NaCl. The *IE*% values obtained from weight loss measurements were lower than those gained by electrochemical technique at same condition. This difference is possibly due to the shorter corrosion time in the electrochemical tests than that in weight loss measurements [71].



**Figure 5.** Potentiodynamic polarization curves for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of different concentrations of single BBB at 25 °C ± 1: blank (-◇-); 0.005 mM BBB (-★-); 0.01 mM BBB (-○-); 0.04 mM BBB(-●-); 0.16 mM BBB (-□-); 0.50 mM BBB(-■-).



**Figure 6.** Potentiodynamic polarization curves for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution with the addition of different concentrations of BBB without and with addition of 0.1 M NaCl at 25 ± 1 °C: blank(-◇-); 0.1 M NaCl(-☆-); 0.1 M NaCl + 0.005 mM BBB (-★-); 0.1 M NaCl + 0.01 mM BBB (-○-); 0.1 M NaCl + 0.04 mM BBB (-●-); 0.1 M NaCl + 0.16 mM BBB (-□-); 0.1 M NaCl + 0.50 mM BBB (-■-).

### 3.5. Explanation of the synergistic inhibition

BBB is a kind of N-heterocyclic compound, which contains four nitrogen atoms with lone-pair electrons and conjugate system. In 0.25 M H<sub>2</sub>SO<sub>4</sub> solution, BBB may be protonated, leading to positive charge in molecule. BBB might be protonated as follows:



In the acid media, positive charges exist on mild steel surface [72, 73]. Due to the electrostatic repulsive interaction, it is difficult for the protonated BBB to reach the positively charged mild steel surface directly, this is why single BBB shows low inhibition efficiency for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution without addition of NaCl. The obtained results from weight loss measurements and electrochemical methods could be explained that in the presence of NaCl, the specific adsorption of chloride ion causes the negatively charged surface of mild steel. Chloride ion has greater tendency to be adsorbed on mild steel surface and is responsible for the synergistic inhibition between BBB and NaCl. The protonated BBB are then adsorbed by electrostatic attraction on the mild steel surface where Chloride ions already are adsorbed, followed by the transference of electron from N atom and conjugate system of BBB to the empty d-orbital of iron atom to form coordinate bond at the mild steel/solution interface (chemisorption). The stable adsorption of BBB cations and chloride ion on mild

steel leads to greater surface coverage and therefore better inhibition effect. Chloride ion to promote the physical adsorption and chemical adsorption is the exact reason why synergism occurs [74]. Another probable reason for the synergistic inhibition of chloride ions with BBB in 0.25 M H<sub>2</sub>SO<sub>4</sub> is that the adding chloride ion lowers the free water molecule on mild steel surface, leading to the BBB molecules increasing [75]. Therefore, the complex of BBB and 0.1 M NaCl suppressed the mild steel corrosion drastically in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution.

#### 4. CONCLUSION

1. Single BBB suppressed mild steel corrosion in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution, inhibition efficiency increases with increasing concentration of BBB, and corrosion rate presents the opposite trend. The inhibition efficiency of BBB is enhanced by the addition of smaller concentration of BBB due to the increase in surface coverage values of BBB in the presence of chloride ions. At any concentration, the inhibition efficiency of BBB-NaCl mixture is higher than that of single BBB. This may be the result that the presence of NaCl increases the electrostatic interaction of BBB cations, indicating there is a synergistic inhibition for mild steel corrosion in sulfuric acid. The BBB-NaCl mixture can be used as a more excellent inhibitor for mild steel corrosion in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution.

2. The addition of single BBB and BBB-NaCl mixture decreased the current density of mild steel and shift no obvious corrosion potential to anodic or cathodic direction, single BBB and BBB-NaCl mixture are both mixed-type inhibitors for mild steel in 0.25 M H<sub>2</sub>SO<sub>4</sub> solution. The weight loss results are in good agreement with electrochemical results.

3. The adsorptions of single BBB and BBB-NaCl mixture onto mild steel surface obey Langmuir adsorption isotherm. The adsorptions are spontaneous process in which electron transfers from BBB molecule to d-orbital of iron to form coordinate bond (chemisorption). Compared with single BBB, the mixture of BBB and NaCl exhibits a stronger tendency to adsorb onto mild steel surface, since the values of adsorption free energy for the mixture are more negative than that for single BBB and the adsorption equilibrium constant for the mixture is larger than that for single BBB.

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