Research Article

Inhibition of Mild Steel Corrosion by 3-Benzoylmethyl Benzimidazolium Hexafluoroantimonate in Acidic Solution

Ayssar Nahle, Ideisan I. Abu-Abdoun, and Ibrahim Abdel-Rahman

Department of Chemistry, College of Sciences, University of Sharjah, P.O. Box 27272, Sharjah, UAE

Correspondence should be addressed to Ayssar Nahle, anahle@sharjah.ac.ae

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The corrosion inhibition of mild steel in 1 M HCl solution by a synthesized compound (3-benzoylmethyl benzimidazolium hexafluoroantimonate) was investigated electrochemically and by weight loss experiments. The concentration of this inhibitor ranged from $5 \times 10^{-7}$ M to $5 \times 10^{-4}$ M. The effect of temperature (from 303 to 343 K) and concentrations (from $5 \times 10^{-7}$ M to $5 \times 10^{-4}$ M) were investigated. The percentage inhibition increased with the increase of the concentration of the inhibitor and reached about 98% at the concentration of $5 \times 10^{-4}$ M at 303 K. The percentage inhibition decreased with the increase of temperature. The thermodynamic parameters for the adsorption of this inhibitor on the metal surface were calculated. This compound was found to be a very good corrosion inhibitor due to the presence of nitrogen in benzimidazole and phenyl ring.

1. Introduction

The corrosion of metals is a serious problem in many industries, installations, and civil services such as water and sewage supplies. One of the most useful and practical methods that used to control and protect metals against corrosion is the use of inhibitors, especially in acidic media. Not only the costs due to corrosion increase rapidly, but also the efficiency of the plants and the quality of the products are also reduced.

Most inhibitors are organic compounds containing polar groups strongly adsorbed on the metal surface [1, 2]. These inhibitors, which include the organic N, P, S, and OH groups, are known to be similar to catalytic poisons, as they decrease the reaction rate at the metal/solution interface without, in general, being involved in the reaction considered. It is generally accepted that most organic inhibitors act via adsorption at the metal/solution interface. The mechanism by which an inhibitor decreases the corrosion current is achieved by interfering with some of the steps for the electrochemical process.

The corrosion inhibition of mild steel in aggressive acidic solutions has been widely investigated. In industries, hydrochloric acid solutions are often used in order to remove scale and salts from steel surfaces, and cleaning tanks and pipelines. This treatment may be prerequisite for coating by electroplating, galvanizing, or painting techniques. The acid must be treated to prevent an extensive dissolution of the underlying metal. This treatment involves the addition of some organic inhibitors to the acid solution that adsorb at the metal/solution interface by displacing water molecules on the surface and forming a compact barrier film.

Nitrogen-containing compounds as metal corrosion inhibitors have been studied thoroughly by many authors. These compounds included benzimidazole and imidazole derivatives [3–13], bipyrazole [14], stilbazo1 [15], quaternary ammonium salts [16–23], polyaminobenzoquinone polymers [24], substituted aniline-N-salicylidenes [25], amides [26], heterocyclic compounds [27, 28], and cationic surfactants [29, 30]. Other authors worked on phosphorus-containing and sulfur-containing inhibitors [15, 31–39]. Other studies involved the effect of addition of some ions on the inhibition efficiency of some organic compounds. These ions included chromium [40], iodide [41–43], and chloride [10, 44]. Structural effect of organic compounds as corrosion inhibitors was also studied [8, 42, 43, 45–47]. In all these studies, the nitrogen, phosphorous, and sulfur atom(s) in the compounds as well as the unsaturated double bonds like phenyl rings showed to be able to adsorb very well on the
metal surface and form protective layer, which in turn increased the corrosion inhibition with the increase in the concentration of the inhibitor, in some cases reaching 99% inhibition [15, 18, 36, 37].

No studies have been reported on 3-benzoylmethyl benzimidazolium hexafluoroantimonate (BMBI) (Scheme 1), in terms of studying both the electrochemical and the temperature effect on the corrosion inhibition of mild steel in 1.0 M HCl solution. Mild steel was chosen in our studies since high temperature aggressive acids are widely used in industries in connection to mild and low alloy steels.

The aim of this work is

(i) to synthesize a high percentage yield of pure 3-benzoylmethyl benzimidazolium hexafluoroantimonate (BMBI);

(ii) to study, using potentiodynamic and weight loss measurements, the effect of temperature on the corrosion inhibition of mild steel in 1.0 M HCl solution by BMBI and to calculate the thermodynamic parameters.

The output of this study is intended to be the building block or the nucleus for a new family or group of imidazole onium derivatives in all studies of corrosion inhibitors.

2. Experimental Details

2.1. Synthesis of 3-Benzoylmethyl Benzimidazolium Hexafluoroantimonate (BMBI). The 3-benzoylmethyl benzimidazolium bromide salt (3) was prepared by refluxing an equimolar mixture of the 1-vinylimidazole and phenacyl bromide (2) in acetone as follows.

2.50 grams (0.021 mol) from benzimidazole (1) and 4.20 grams from phenacyl bromide (0.023 mol) (2), in 100 mL acetone, were refluxed for two hours. After cooling to room temperature, a crystalline solid of salt (3) was collected by filtration then washed with excess diethyl ether and dried.

The bromide salt (3) was converted to the hexafluoroantimonate salt (4) by treatment with potassium hexafluoroantimonate (KSBF_{6}) in methanol/water mixture 70/30% by volume. After stirring for 20 min, the reaction product was filtered, washed several times with water then with diethyl ether, and dried under vacuum at room temperature. Dissolution in chloroform and addition of excess diethyl ether gave the pure hexafluoroantimonate salt in 80 yield percent as shown in Scheme 2.

3. Electrochemistry

3.1. Electrode Preparation (Electrochemistry). A 5 mm diameter piece cut from a mild steel rod (IS 226 containing 0.18% C, 0.6% Mn, and 0.35% Si) supplied by "Reliable Steel Traders," Sharjah, UAE, formed the working electrode and was mounted, using Araldite epoxy resin, in a glass tube that fits in the electrochemical cell. Prior to each experiment, the working mild steel electrode was abraded using a series of carborundum papers starting with 600 grades and ending with 1200 grades. The electrode surface was then polished with 0.3 μm alumina on cloth, washed with deionized distilled water, and rinsed with pure ethanol before being transferred to the electrochemical cell that contained deaerated fresh electrolyte.

3.2. Instrumentation (Electrochemistry). The electrochemical cell (Figure 1) consisted of a mild steel working electrode (WE), a saturated calomel electrode (SCE) as a reference electrode (RE), and platinum gauze counter electrode (CE). Prior to each experiment, the electrolyte was deaerated by nitrogen bubbling. The cell was designed in a way that the nitrogen was allowed to escape into the solution, precluding its collection at the electrode surface.

In order to protect the working electrode from any substance that may be produced at the counter electrode during the electrochemical reactions, the counterelectrode compartment was separated from the working-electrode compartment with a glass frit. The following electrochemical instrument was used a PC controlled AUTO-LAB PGSTAT128N Modular Potentiostat (electrochemical workstation) (supplied from Metrohm) capable of driving currents up to ±800 mA with an output potential across the cell of up to ±10 V.

3.3. Measuring Procedure (Electrochemistry). Electrochemical corrosion measurements (Tafel plots) were carried out on the mild steel electrode, prepared as described before, in 1.0 M HCl and in 1.0 M HCl containing various concentrations of the prepared BMBI inhibitor. The concentration of the inhibitor ranged from 5×10^{-7} M to 5×10^{-4} M. Due to the restricted solubility of BMBI inhibitor, higher concentrations could not be prepared.

The electrode potential was scanned between over potentials of −100 mV to +100 mV versus SCE at a sweep rate of 1 mV·s^{-1}.

3.4. Results and Discussions (Electrochemistry). Figure 2 shows the anodic and cathodic polarization curves (Tafel plot) of the mild steel electrode in deaerated 1.0 M HCl solution with and without the addition of various concentrations of 3-benzoylmethyl benzimidazolium hexafluoroantimonate (BMBI). The presence of the inhibitor affected both the anodic and cathodic branches of the curve as it can be clearly seen in Figure 2. The corrosion current was found to decrease with the increase of the concentration of BMBI inhibitor as shown in Table 1. In the absence of inhibitor (in
Figure 1: Electrochemical cell.

Scheme 2: Synthesis of 3-benzoylmethyl benzimidazolium hexafluoroantimonate.

1.0 M HCl), the corrosion current was found to be 0.74 mA, which decreased sharply to 0.026 mA at $5 \times 10^{-4}$ M of BMBI inhibitor in 1.0 M HCl (Table 1).

The percentage inhibition values of BMBI at various concentrations in 1.0 M HCl were calculated according to the following equation (1) and the results are shown in Table 1:

\[
\text{Percentage Inhibition} = \frac{(I_{\text{Corr.}})_{\text{Uninh.}} - (I_{\text{Corr.}})_{\text{Inh.}}}{(I_{\text{Corr.}})_{\text{Uninh.}}} \times 100, 
\]

where $(I_{\text{Corr.}})_{\text{Uninh.}}$ is corrosion current in the uninhibited solution and $(I_{\text{Corr.}})_{\text{Inh.}}$ is corrosion current in inhibited solution.

Figure 3 shows the plot of the percentage inhibition versus the concentration of BMBI. In this figure, the percentage inhibition increases gradually from about 54% (with $5 \times 10^{-7}$ M inhibitor) to reach about 96% with $5 \times 10^{-4}$ M inhibitor.

4. Effect of Temperature

4.1. Specimen Preparation (Effect of Temperature). Rectangular specimens (1.0 cm $\times$ 2.3 cm $\times$ 0.3 cm) cut from large sheet of 3 mm thick mild steel (IS 226 containing 0.18% C, 0.6% Mn, and 0.35% Si) supplied by “Reliable Steel Traders,” Sharjah, UAE, were used for weight loss measurements. A 2 mm diameter hole was drilled close to the upper edge of the specimen and served to be hooked with a glass rod for immersion purposes. Prior to each experiment, the specimens were polished with 600 grade emery paper, rinsed with distilled water, degreased with acetone, dried, and finally weighed precisely on an accurate analytical balance.
Table 1: Tafel corrosion currents and percent inhibitions of 3-benzoylmethyl benimidazolium hexafluoroantimonate (BMBI) at various concentrations in 1.0 M HCl at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>1.0 M HCl</th>
<th>1.0 M HCl + 5 × 10⁻⁷ M BMBI</th>
<th>1.0 M HCl + 5 × 10⁻⁶ M BMBI</th>
<th>1.0 M HCl + 5 × 10⁻⁵ M BMBI</th>
<th>1.0 M HCl + 5 × 10⁻⁴ M BMBI</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{corr}} ) versus SCE</td>
<td>−0.459</td>
<td>−0.472</td>
<td>−0.472</td>
<td>−0.461</td>
<td>−0.583</td>
</tr>
<tr>
<td>( i_{\text{corrosion}} ) mA</td>
<td>0.74</td>
<td>0.34</td>
<td>0.27</td>
<td>0.16</td>
<td>0.026</td>
</tr>
<tr>
<td>Percent Inhibition</td>
<td>—</td>
<td>54.05</td>
<td>63.51</td>
<td>78.38</td>
<td>96.49</td>
</tr>
</tbody>
</table>

**Figure 2:** Anodic and cathodic polarization curves of mild steel in an uninhibited 1.0 M HCl solution and in 1.0 M HCl containing various concentrations of 3-benzoylmethyl benimidazolium hexafluoroantimonate (BMBI) at ambient temperature. (1) 1.0 M HCl; (2) 1.0 M HCl + 5 × 10⁻⁷ M inhibitor; (3) 1.0 M HCl + 5 × 10⁻⁶ M inhibitor; (4) 1.0 M HCl + 5 × 10⁻⁵ M inhibitor; (5) 1.0 M HCl + 5 × 10⁻⁴ M inhibitor.

4.2. Instrumentation (Effect of Temperature). The experimental setup consisted of a 250 mL round bottom flask fitted with a reflux condenser and a long glass rod on which the specimen was hooked and in turn immersed in a thermally controlled water bath.

4.3. Measuring Procedure (Effect of Temperature). The flask was filled with 100 mL of 1.0 M HCl solution either with or without BMBI of various concentrations, then placed in water bath. As soon as the required working temperature was reached, the precisely weighed mild steel specimen was immersed in the solution and left there for exactly six hours, after which the sample was removed, rinsed with distilled deionized water, degreased with acetone, dried, and finally weighed precisely on an accurate analytical balance. This procedure was repeated with all the samples with a variety of inhibitor concentrations ranging from 5 × 10⁻⁷ M up to 5 × 10⁻⁴ M and at temperatures ranging from 303 K to 343 K.

4.4. Results and Discussions (Effect of Temperature). Weight loss corrosion tests were carried out on the mild steel in 1 M HCl in the absence and presence of (BMBI) over a period of 6 hours. Table 2 represents the corrosion rates \([\text{mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}]\) and the percentage efficiencies [%] for the studied inhibitor with concentrations varying from 5 × 10⁻⁷ M to 5 × 10⁻⁴ M at 303, 313, 323, 333, and 343 K, respectively. The percentage efficiency was calculated according to the following expression (2):

\[
\% \text{Inhibition} = \frac{W_{\text{Uninh.}} - W_{\text{Inh.}}}{W_{\text{Uninh.}}} \times 100, \tag{2}
\]

where \(W_{\text{Uninh.}}\) is corrosion rate without inhibitor; and \(W_{\text{Inh.}}\) is corrosion rate with inhibitor.

Figures 4 and 5 show the plots of the corrosion rate of (BMBI) as a function of concentration at 303, 313, 323, 333, and 343 K extracted from Table 2. At 303 K (Table 2, Figure 4), the corrosion rate dropped sharply from the value 0.961 mg cm⁻² h⁻¹ (1 M HCl in the absence of the
Table 2: Effect of concentration of 3-Benzoylmethyl benzimidazolium hexafluoroantimonate (BMBI) on the corrosion rate (mg·cm$^{-2}$·h$^{-1}$) and percentage efficiency of mild steel in 1.0 M HCl at various temperatures.

<table>
<thead>
<tr>
<th>Concentration of Inhibitor</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
<th>343</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>0.961</td>
<td>—</td>
<td>1.394</td>
<td>—</td>
<td>4.671</td>
</tr>
<tr>
<td>1 M HCl + 5 × 10$^{-7}$ M</td>
<td>0.363</td>
<td>62.3</td>
<td>0.686</td>
<td>50.8</td>
<td>2.673</td>
</tr>
<tr>
<td>1 M HCl + 5 × 10$^{-6}$ M</td>
<td>0.229</td>
<td>76.2</td>
<td>0.508</td>
<td>63.6</td>
<td>2.177</td>
</tr>
<tr>
<td>1 M HCl + 5 × 10$^{-5}$ M</td>
<td>0102</td>
<td>89.4</td>
<td>0.182</td>
<td>86.9</td>
<td>1.179</td>
</tr>
<tr>
<td>1 M HCl + 5 × 10$^{-4}$ M</td>
<td>0.018</td>
<td>98.1</td>
<td>0.052</td>
<td>96.0</td>
<td>0.256</td>
</tr>
</tbody>
</table>

Figure 4: Effect of concentration of 3-Benzoylmethyl benzimidazolium hexafluoroantimonate (BMBI) on the corrosion rate (mg·cm$^{-2}$·h$^{-1}$) of mild steel in 1.0 M HCl at various temperatures.

In Figure 4, the same behavior is shown as in Figure 4. The corrosion rate at 333 and 343 K are shown as a function of the concentration of (BMBI). It can be clearly seen that the presence of the (BMBI) inhibitor at these high temperatures has acted as a corrosion inhibitor reaching a percent inhibition of 81.0% and 71.5% when 5 × 10$^{-4}$ M inhibitor was employed at 333 K and 343 K, respectively.

Figure 5 shows the plots of the % inhibition versus the concentration of the inhibitor at temperatures of 303, 313, 323, 333, and 343 K, respectively. This figure showed that the % inhibition increased as the temperature decreased at the same inhibitor concentration. The presence of the inhibitor has greatly increased the % inhibition at all temperatures.

In Figure 5, the same behavior is shown as in Figure 4. The corrosion rate at 333 and 343 K are shown as a function of the concentration of (BMBI). It can be clearly seen that the presence of the (BMBI) inhibitor at these high temperatures has acted as a corrosion inhibitor reaching a percent inhibition of 81.0% and 71.5% when 5 × 10$^{-4}$ M inhibitor was employed at 333 K and 343 K, respectively.

Figure 6 shows the plots of the % inhibition versus the concentration of the inhibitor at temperatures of 303, 313, 323, 333, and 343 K, respectively. This figure showed that the % inhibition increased as the temperature decreased at the same inhibitor concentration. The presence of the inhibitor has greatly increased the % inhibition at all temperatures.
The data obtained from the weight loss measurements (Table 3) were plotted in accordance to Arrhenius equation (3):

\[ \ln \text{rate} = -\frac{E_a}{RT} + \text{const.} \]  

where \( E_a \) is activation energy [kcal·mol\(^{-1}\)], \( R \) is gas constant [kcal·mol\(^{-1}\)·K\(^{-1}\)], \( T \) is absolute temperature [K], and const. is constant.

<table>
<thead>
<tr>
<th>System</th>
<th>Activation energy, ( E_a ) (kcal·mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>18.27</td>
</tr>
<tr>
<td>1 M HCl + BMBI</td>
<td>33.06</td>
</tr>
<tr>
<td>5 × 10(^{-4}) M</td>
<td>18.27</td>
</tr>
<tr>
<td>5 × 10(^{-5}) M</td>
<td>18.27</td>
</tr>
<tr>
<td>5 × 10(^{-6}) M</td>
<td>26.43</td>
</tr>
<tr>
<td>5 × 10(^{-7}) M</td>
<td>23.35</td>
</tr>
<tr>
<td>5 × 10(^{-8}) M</td>
<td>22.31</td>
</tr>
</tbody>
</table>

Figure 7 represents the Arrhenius plot of the corrosion of mild steel in 1 M HCl solution (\( \ln \) corrosion rate as a function of \( 1/T \)) with and without the presence of (BMBI) at concentrations ranging from \( 5 \times 10^{-4} \) M to \( 5 \times 10^{-7} \) M. From this figure, the slope \( (-E_a/R) \) of each individual line was determined and used to calculate the activation energy according to (3) and taking \( R = 1.987 \times 10^{-3} \) kcal·mol\(^{-1}\)·K\(^{-1}\) (Table 4). The increase of concentration of (BMBI) (from \( 5 \times 10^{-7} \) M to \( 5 \times 10^{-4} \) M) increased the activation energies for the corrosion of mild steel in 1 M HCl (initially 18.27 kcal·mol\(^{-1}\)) (Table 4). The increase in the activation energies for the corrosion is attributed to a decrease in the adsorption of the inhibitor on the metal surface as the temperature increased; subsequently, an increase in the corrosion rate will result due to the greater exposed area of the metal surface to the acid.

The results in Table 4 show that the activation energy \( (E_a) \) for the corrosion of mild steel in the presence of the inhibitor is higher compared to the activation energy in the absence of
Table 5: Effect of concentration of 3-benzoylmethyl benzimidazolium hexafluoroantimonate on surface coverage for mild steel in 1.0 M HCl at various temperatures.

<table>
<thead>
<tr>
<th>Concentration of inhibitor</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
<th>343 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl + 5 \times 10^{-7} M</td>
<td>0.623</td>
<td>0.508</td>
<td>0.428</td>
<td>0.302</td>
<td>0.168</td>
</tr>
<tr>
<td>1 M HCl + 5 \times 10^{-6} M</td>
<td>0.762</td>
<td>0.636</td>
<td>0.534</td>
<td>0.459</td>
<td>0.344</td>
</tr>
<tr>
<td>1 M HCl + 5 \times 10^{-5} M</td>
<td>0.894</td>
<td>0.869</td>
<td>0.748</td>
<td>0.637</td>
<td>0.550</td>
</tr>
<tr>
<td>1 M HCl + 5 \times 10^{-4} M</td>
<td>0.981</td>
<td>0.960</td>
<td>0.945</td>
<td>0.810</td>
<td>0.715</td>
</tr>
</tbody>
</table>

Figure 8: Effect of concentration of 3-benzoylmethyl benzimidazolium hexafluoroantimonate (BMBI) on the surface coverage of mild steel in 1.0 M HCl at various temperatures.

It was concluded that all inhibitors were adsorbed on the mild steel surface according to Temkin isotherm:

$$-2a\theta = \ln KC,$$

where $a$ is molecular interaction constant, $\theta$ is degree of coverage, $K$ is equilibrium constant for the adsorption reaction, and $C$ is concentration of the inhibitor.

The equilibrium constant for the adsorption reaction, $K$, is related to the standard free energy of adsorption via the following equation given by Damaskin et al. [1]:

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G}{RT}\right),$$

where $K$ is equilibrium constant for the adsorption reaction, 55.5 is concentration of water [mol·L$^{-1}$], $\Delta G$ is standard free energy [kcal·mol$^{-1}$], $R$ is gas constant [kcal·mol$^{-1}$], and $T$ is absolute temperature [K].

According to (4), the straight lines shown in Figure 8 will have the following slopes and intercepts:

Slope = $-\frac{1}{2a}$, (6)

Intercept = $-\frac{1}{2a} \ln K$. (7)

Combination of (6) and (7) leads to the following relationship:

Intercept = Slope × (ln $K$), (8)

from which the equilibrium constant for the adsorption reaction, $K$, can be calculated:

$$K = e^{(\text{Intercept/slope})}.$$ (9)

The standard free energy of adsorption of the inhibitor, $\Delta G^0$, can be calculated from the results in Figure 8 used to calculate the equilibrium constant, $K$, and (5) at various temperatures (303 to 343 K).

The enthalpy of adsorption, $\Delta H^0$, for the inhibitor can be calculated from the following equation:

$$\Delta H^0 = E_a - RT.$$ (10)

The entropy, $\Delta S^0$, can be calculated at various temperatures for the inhibitor using the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0.$$ (11)
3-Benzoylmethyl benzimidazolium hexafluoroantimonate is a potential corrosion inhibitor since it contains not only nitrogen atom, but also phenyl and benzimidazole ring together with carbonyl group (C=O). It was apparent from the molecular structure that this compound would be adsorbed onto the metal surface through the lone pair of electron of nitrogen and oxygen and pi electrons of the aromatic rings (phenyl and benzimidazole) and the carbonyl group.

The percentage of inhibition in the presence of this inhibitor decreased as the temperature increased which indicates that physical adsorption was the predominant inhibition mechanism, because the quantity of adsorbed inhibitor decreases with increasing temperature.

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**References**


