



# Corrosion inhibition of mild steel by bromide-substituted imidazoline in hydrochloric acid



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## ABSTRACT

A new imidazoline compound, 2-(2-tribromomethyl-4,5-dihydro-imidazol-1-yl)-ethylamine (3-IM) was synthesized and its inhibitory effect on the corrosion of mild steel in 0.5 M HCl solution was examined by weight loss, potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS). The experimental results show that 3-IM behaves as a mixed-type inhibitor and the inhibition efficiency increases with the increasing compound concentrations. The adsorption actions of 3-IM molecules are well fitted by Langmuir isotherm, while the protection property of the adsorptive layer decreases as the temperature increases.

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## 1. Introduction

Mild steel, an important industrial material, is widely used for pipelines and vessels where some inorganic scales easily form. Therefore, a couple of acid solutions including hydrochloric acid are employed to clean scales in those equipments [1,2]. However, this process may cause the corrosion of metal, which leads to financial losses and safety problems. The usage of inhibitors is an effective way to protect iron against aggressive media [3–6]. The corrosion behavior of metal can be controlled by many natural extracts and synthetical compounds such as bamboo leaves [7], henna [8,9], coffee [10], *Myrtus communis* [11], Schiff bases [12–14], pyrimidine [15–17], thiazole [18–20], and imidazoline [21–24]. Chemical structures of those functional compounds are often related with O, S, N atoms, and multiple bonds which are all electron-rich groups [25,26].

The inhibitory performance of organic compounds is due to the adsorptive layer forming between the molecules with lone electron pair and/or  $\pi$  electrons and the surface metal atoms with unoccupied *d*-orbitals [27]. For the moment, quantum chemical calculation acts as a useful tool to study the relationship between molecular structures and inhibition efficiencies; thus, it can provide theoretical support in searching for new inhibitors [28]. The inhibition abilities of compounds are deeply impacted by the configurations of the adsorbed molecules on metal surface. Molecular dynamics (MD) method plays an important role in studying the adsorption

behavior of inhibitors since it can simulate the adsorption system at a molecular level [29].

To build a system of halogen-substituted imidazoline inhibitors, we investigated the inhibiting performance of bromide-containing compound (Fig. 1) in 0.5 M HCl solution by weight loss, potentiodynamic polarization measurements and electrochemical impedance spectroscopy (1-IM and 2-IM have been already studied in our previous report). Therefore, this work is also aimed to compare the inhibition abilities of above-mentioned compounds.

## 2. Experimental details

### 2.1. Materials and samples preparation

The synthesis of bromide-substituted compound (3-IM) was conducted according to the published method [30]. The molecular structure of 3-IM was confirmed by using <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR spectroscopic methods and the purity of production was guaranteed by identifying atoms (C and H) and melting point.

3-IM: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz),  $\delta$ , *J*: 3.32, 9.0 Hz (t, 2H, –C=N–CH<sub>2</sub>–), 3.30, 12 Hz (t, 2H, –CH<sub>2</sub>–N–), 2.56, 15 Hz (t, 2H, –CH<sub>2</sub>–C–N–), 2.52 3 Hz (t, 2H, –C=N–C–CH<sub>2</sub>–N–), 7.4 (s, 2H, –NH<sub>2</sub>). FT-IR (KBr)  $\nu$ : 3362, 1660, 1556, 1484, 1322, 1114, 826, 602 cm<sup>–1</sup>. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 300 MHz)  $\delta$ : 160.8 (C=N), 116.2 (CF<sub>3</sub>), 56.2 (C–NH<sub>2</sub>), 46.4 (N–C<sub>ring</sub>), 41.5 (C–C–NH<sub>2</sub>), 37.6 (C<sub>ring</sub>–N=). Melting point: 209.4–210.2 °C.

The blank solution of 0.5 M HCl was prepared by diluting the analytical grade HCl (37 wt.%) with double-distilled water. In this work, the inhibitor concentrations are 0.1, 0.5, 1, 1.5 and 2 mM. Mild

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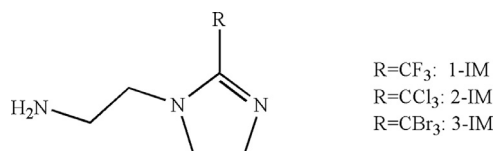


Fig. 1. Chemical structures of halogen-substituted imidazoline compounds.

steel materials (0.17 wt.% C, 0.37 wt.% Mn, 0.20 wt.% Si, 0.03 wt.% S, 0.01 wt.% P and balance Fe) were mechanically treated to obtain a cuboid sheet (5.00 cm × 2.50 cm × 0.20 cm) for weight loss tests. In electrochemical section, the test electrode was prepared by embedding the mild steel in epoxy resin with a surface area of 0.5 cm<sup>2</sup> exposed to the corrosive solution.

## 2.2. Weight loss experiments

Weight loss measurements were performed by placing metallic samples in an open glass cell with 500 mL of 0.5 M HCl solution. Mild steel specimens were immersed for 8 h in the electrolyte with and without inhibitors at different temperatures (30, 40, 50, 60, and 70 °C).

## 2.3. Electrochemical measurements

The electrochemical tests were performed by using a standard three-electrode cell in which the reference electrode is a saturated calomel electrode (SCE) coupled to a Luggin capillary and the support electrode is a platinum mesh. Before testing, the working electrode (WE) was abraded with emery paper (500, 1000, 2000 grade), cleaned in ethanol, washed with ultrapure water and dried at room temperature.

Electrochemical experiments were conducted at 30 °C in a glass beaker with 100 mL of 0.5 M HCl solution in the absence and presence of 3-IM at the following concentrations: 0.1, 0.5, 1, 1.5, and 2 mM. Prior to all electrochemical tests, WE was immersed in the electrolyte for 1 h to obtain a stable open-circuit potential (OCP). The potentiodynamic polarization curves were drawn by scanning the studied potential range from –700 mV to –300 mV (vs. SCE) at a rate of 1 mV/s. At open-circuit potential, electrochemical impedance spectra measurements were performed over a frequency range of 100 mHz to 100 kHz by imposing a sinusoidal alternating current (AC) wave of 5 mV (peak to peak). The test cell was placed in a non-stirred and naturally aerated hydrochloric acid solution and the system temperature was maintained at 30 ± 0.1 °C.

## 2.4. Surface analysis

Scanning electron microscope (SEM) was employed to observe the surface morphologies of samples after 24 h of immersion in 0.5 M HCl solution without and with 1 mM 3-IM at 70 °C. SEM photos of metallic sheets were obtained using JSM-6480 scanning electron microscope in vacuum with 20.0 kV extra high tension (EHT).

## 2.5. Computational methods

In this study, Quantum chemical calculations were performed to obtain theoretical understanding of our findings. With a good accuracy of convergence, a setting of double zeta plus polarization (DNP) and a frequency analysis to ensure that the energy of the calculated framework on the potential surface is minimum, the GGA/BLYP method from density functional theory (DFT) was used to characterize the molecular orbitals of 3-IM.

Molecular dynamics (MD) simulations were performed to study the three-dimensional configurations of adsorbed molecules by running Material Studio 5.5 software. The matrix for the simulation

of adsorption process is Fe (1 1 0) crystal. In a cuboid space (19.86 Å × 19.86 Å × 38.10 Å), MD calculation was conducted to study the interaction between inhibitor molecule and metal surface. The Fe (1 1 0) plane cleaved from Fe crystal was optimized to reach the minimal energy and extended to obtain a proper supercell. A vacuum layer with a thickness of 30 Å was built upon the Fe (1 1 0) surface. Next, the steric skeleton of target molecule was presented and optimized. Locations of Fe atoms were constant while the atoms of the selected molecule could conditionally move during the geometry optimization. Lastly, the simulative adsorption system including the Fe (1 1 0) crystal and the studied molecule was obtained by layer builder, and the dynamic displacement of the inhibitor molecule above metal surface was then driven by polymer consistent force field (PCFF).

The adsorption energy between inhibitor molecules and Fe (1 1 0) surface was calculated as the following formula:

$$E_{interaction} = E_{total} - (E_{surface} + E_{inhibitor}) \quad (1)$$

where  $E_{total}$  is the total energy of the full system containing Fe crystal and the adsorbed molecule,  $E_{surface}$  and  $E_{inhibitor}$  are the energy of the metallic crystal and the free molecule, respectively. The binding energy is related with the interaction energy,  $E_{binding} = -E_{interaction}$ .

## 3. Results and discussion

### 3.1. Weight loss experiments

The inhibiting effect of 3-IM at different concentrations was determined in 0.5 M HCl solution. Table 1 shows the inhibition efficiency ( $\eta$ ) calculated by the following equation [31]:

$$\eta = \frac{W^0 - W}{W^0} \times 100\% \quad (2)$$

where  $W^0$  and  $W$  indicate the corrosion rates of steel samples without and with the protection of an inhibitor, respectively. Results from Table 1 show the good inhibition performance of 3-IM for the corrosion of mild steel in acid solution at relatively high temperatures. For instance, the inhibitory efficacy of 3-IM in each concentration at 50 °C is greater than 80%. The inhibition percentage increases as additive contents increase, suggesting more inhibitor molecules are adsorbed to form a self-assembly layer on metal surface [32]. We can observe the obvious effect of temperatures on the inhibitory property of 3-IM according to the data in Table 1. Increasing temperature accelerates the anodic dissolution of iron and blocks the adsorption of organic molecules by speeding the cathodic reaction to product a mass of hydrogen. With respect to the high efficiency at 30 °C, 90%, the efficiency of 0.1 mM 3-IM at 70 °C drops to 74%.

### 3.2. Open circuit potential (OCP) curves

Fig. 2 shows the OCP–time curve for mild steel electrode immersed in 0.5 M HCl solution in the absence and presence of 1 mM 3-IM. An obvious drop of the potential in early 10 min can be observed, which implies the depassivation phenomenon occurring on the electrode surface [33]. 40 min later, the simultaneous processes including the decomposition of metal and the adsorption of inhibitor reach balance, and thus the function line tends to be horizontal. Up to 60 min, the curve still keeps straight so that we choose 1 h for the immersion time.

### 3.3. Potentiodynamic polarization study

Fig. 3 shows the Tafel polarization curves for the metallic electrode immersed in 0.5 M HCl solution in the absence and presence of different concentrations of 3-IM. With respect to the polarization diagram in the blank solution, the ones in inhibited solutions with the addition of 3-IM shift downward. That observation allows us to

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