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Electrochemical impedance spectroscopy and electrochemical noise measurements as tools to evaluate corrosion inhibition of azole compounds on stainless steel in acidic media

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ABSTRACT

The corrosion inhibition function of two azole derivatives namely benzotriazole (BTR) and benzothiazole (BNS) on stainless steel in 1 M HCl was investigated using electrochemical techniques and SEM surface analysis as well. In consistency with the data obtained from EIS and polarization curves, electrochemical current noise transient analysis, noise resistance and characteristic charge from shot noise theory indicated effectiveness of the inhibitors. The corrosion damage mitigation was also confirmed through SEM in the presence of BNS. To remove the DC trend from noise data, the appropriate *p* value was proposed based on the correlation with polarization and EIS data.

1. Introduction

Metals face acid solutions in industrial scale during oil well acidification, acid pickling, acid descaling, etc. [1–3]. Hydrochloric and sulfuric acids are the widely used solutions for these applications [4]. Many grades of stainless steels are susceptible to localized corrosion in Cl^- containing acidic media [5]. In this sense, organic inhibitors are employed as one of the most practical methods for corrosion protection [6]. The inhibition efficiency of organic inhibitors is reportedly connected to the formation of a layer on the metal surface through adsorption leading to blockage of active sites [7–9]. The phenomenon, which is strongly dependent on the physicochemical properties of the metal surface as well as inhibitor molecule structure, occurs through interaction between unoccupied orbitals of metal surface and electron donator parts of the inhibitor molecules. Hence, the organic molecules containing heteroatoms such as nitrogen and sulfur, aromatic rings and π bonds, are believed to function as effective inhibitors in acid solutions [10–12].

The corrosion inhibition mechanisms of different compounds have been already studied through taking advantage of several electrochemical techniques and surface analysis methods as well. Common electrochemical tools, in particular EIS and potentiodynamic polarization methods, have been widely employed to provide a better understanding of inhibition performance [13–15]. In the recent decade, an increasing interest toward applying brand new techniques such as electrochemical noise method (EN) among corrosion researchers could be spotted. This technique has been used in corrosion monitoring [16,17], evaluation of localized corrosion [18,19], investigation of organic coatings [20–22], and evaluation of inorganic anticorrosive pigments [23]. However, few data has been released regarding evaluation of the behavior of organic inhibitors in acid solutions using EN [24,25].

Among organic compounds, benzotriazole (BTR) and benzothiazole (BNS) have proved to be effective inhibitors on mild steel [26] and copper [27] in acid solutions. In the case of stainless steel, although the performance of BTR in acidic media has been studied [28], there is no report about the inhibition of BNS in acid solutions.

The scope of this work is to evaluate the corrosion behavior of stainless steel in hydrochloric acid solutions containing BNS and BTR using electrochemical methods and SEM surface analysis. In this regard, different aspects of EN parameters are focused to

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assess function of the corrosion inhibitors. Furthermore, it is intended to seek the correlation between EN data and the parameters obtained from EIS and polarization curves.

2. Experimental

2.1. Materials

The chemical structure of the organic inhibitors used in this work is shown in Fig. 1. The compounds in analytical grade were purchased from Merck and used without further purification. In order to prepare the inhibited solutions, different concentrations of the inhibitors were added to 1 M HCl solutions. All electrochemical measurements were performed on the austenitic stainless steel panels (composition wt.%: C:0.04, P:0.08, Si:0.75, Ni:8, Cr:18, Mn:2, N:0.1, S:0.8 and Fe: balance) exposed to the hydrochloric acid solutions containing 0, 100, 200, 300 and 400 ppm (weight/volume) of the corrosion inhibitors at 25 °C ± 2 °C without de-aeration. During immersion time the temperature was kept constant using a water bath. For all electrochemical tests, the stainless steel plates, supplied by Tianjin TISCO & TPCO stainless steel Co. Ltd., were cut as rectangular specimens. The specimen surface was abraded with abrasive papers starting from 80 to 2000 grit size. The samples were rinsed with distilled water and dried in air, then followed by acetone degreasing. One surface of the samples was connected to a copper wire for electrical connection. To seal the edges and back sides of the steel panels, they were covered with a beeswax–colophony mixture, leaving an area of 1 cm^2 unmasked. Meanwhile, each test was carried out using three replicates to ensure repeatability.

2.2. Methods

After 4 h of immersion, all electrochemical measurements were carried out employing Autolab instrument model PGstat 302N. To preform EIS and polarization measurements, a conventional three electrode cell including the prepared stainless steel specimen as working electrode, a Platinum counter electrode and a saturated Ag/AgCl reference electrode was used. EIS measurements were executed at open circuit potential (OCP) within the frequency domain 10 kHz to 0.01 Hz using a sine wave of 10 mV amplitude peak to peak. Polarization curves were provided at a scan rate of 1 mV s^{-1} from −160 mV to +160 mV of OCP.

Electrochemical potential and current noise were simultaneously measured in a freely corroding system employing two nominally identical working electrodes of the same area (preparation method is mentioned in Section 2.1), and a saturated Ag/AgCl reference electrode. The area of each electrode exposed to the solution was about 1.0 cm^2. The three electrodes were immersed in the 1 M HCl solution containing different concentrations of the inhibitors at 25 °C without de-aeration. The reference electrode was placed in the middle of 1-cm distance between the two working electrodes. During the electrochemical measurements, the cell was placed in a Faradic cage to minimize possible external electromagnetic interference. The noise data were recorded for 1024 s at a sampling rate of 1 s. EN measurements were carried out with an apparatus containing a noise module with the input range of ±2.5 V, maximum potential resolution of 760 nV and potential accuracy of 300 μV. The potential and current noise data collected in the time domain were transformed in the frequency domain through the fast Fourier transform (FFT) method. All data analysis was made using NOVA 1.8 software.

The morphology of the sample surface exposed to acid solutions containing 0 and the highest concentration of BNS (400 ppm) was studied using a SEM model Philips XL30. To perform SEM analysis, the samples were immersed in the test solutions for 4 h at 25 °C.

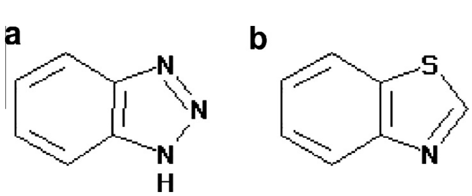

Fig. 1. Molecular structure of (a) benzotriazole (BTR) and (b) benzothiazole (BNS).

3. Results and discussion

3.1. Potentiodynamic polarization measurements

Figs. 2 and 3 depict cathodic and anodic branches of polarization curves for stainless steel panels immersed in the 1 M HCl solutions containing different concentrations of BTR and BNS for 4 h, respectively. From Fig. 2 it is clear that the curves shifted toward lower current densities in the presence of the inhibitors, indicating effective corrosion mitigation in HCl media. Since the influence of the inhibitors on the Tafel slopes of cathodic branches is negligible, one can deduce that BTR and BNS cannot change the mechanism of proton discharge reaction [29]. Therefore, the drop in the cathodic current densities might be linked to blocking the cathodic sites

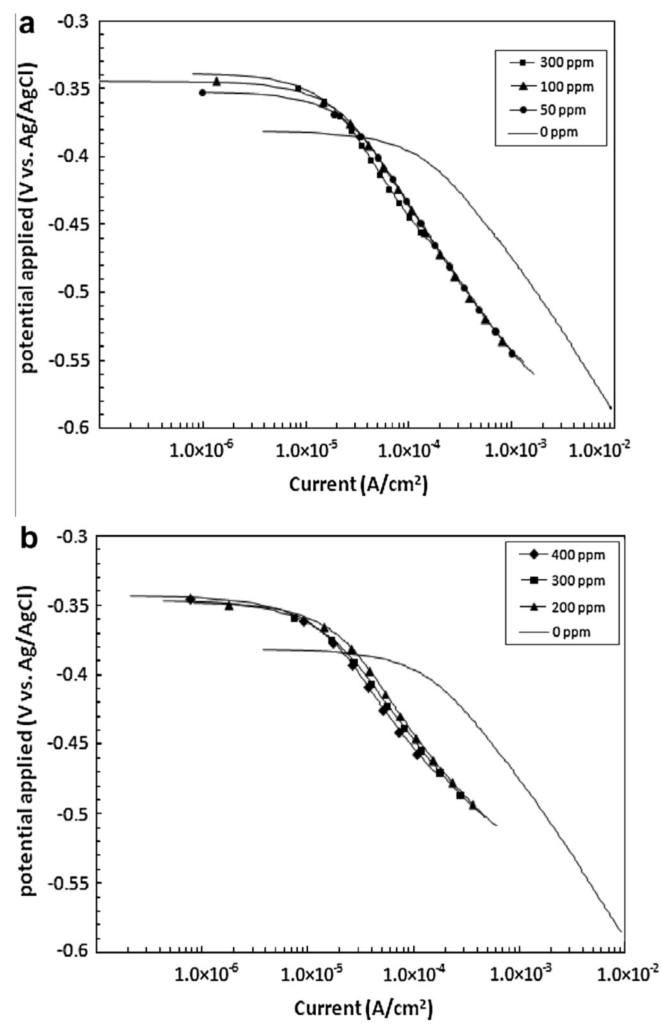

Fig. 2. Cathodic branches of polarization curves of the stainless steel plates after 4-h immersion in 1 M HCl containing different concentrations of (a) BTR and (b) BNS.

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