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Analysis of electrochemical noise (ECN) data in time and frequency domain for comparison corrosion inhibition of some azole compounds on Cu in 1.0 M H_2SO_4 solution

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ABSTRACT

In this study, the corrosion inhibition properties of two similar heterocyclic compounds namely benzotriazole (BTA) and benzothiazole (BNS) inhibitors on copper in 1.0 M H_2SO_4 solution were studied by electrochemical techniques as well as surface analysis. The results showed that corrosion inhibition of copper largely depends on the molecular structure and concentration of the inhibitors. The effect of DC trend on the interpretation of electrochemical noise (ECN) results in time domain was evaluated by moving average removal (MAR) method. Accordingly, the impact of square and Hanning window functions as drift removal methods in frequency domain was studied. After DC trend removal, a good trend was observed between electrochemical noise (ECN) data and the results obtained from EIS and potentiodynamic polarization. Furthermore, the shot noise theory in frequency domain was applied to approach the charge of each electrochemical event (q) from the potential and current noise signals.

1. Introduction

Metals are exposed to acid solutions in industrial applications during acid pickling, acid cleaning and chemical or electrochemical etching [1,2]. Hydrochloric and sulfuric acids are the most common types of aggressive solutions for these applications [3]. So, for the metals exposed to such solutions it is necessary to add corrosion inhibitors in order to hinder the corrosion of metals. Benzotriazole has been regarded as an excellent corrosion inhibitor for different metallic substrate i.e. copper [4], mild steel [5], aluminum [6] and stainless steel [7] due to the presence of three nitrogen atoms in its aromatic ring for a long time. Researchers have reported that benzotriazole has high corrosion inhibition properties by its nitrogen atom at the 3-position of its triazole ring in very acidic media (pH < 1). This means that BTA molecules are predominantly in protonated form ($BTAH^+$) in acidic media. The copper surface has been also found as a positively charged surface in acidic environment. This may be responsible for a decrease in the chemisorption of BTA molecules on the copper surface [8–10]. However, a high corrosion inhibition of BTA has been reported in neutral or alkaline media [11,12]. In order to overcome this problem, researchers have investigated the synergism effects of benzotriazole (as a cationic type of inhibitor in an acidic media) and some anions in sulfuric acid solution on copper [13,14]. As further investigations on this matter, the effect of ring substituted benzotriazole have been examined with the hope of finding proper compounds [10,15,16]. Some researchers have mentioned that compounds with sulfur and nitrogen at the same time in their molecular structures show excellent inhibition performance in comparison with those containing only nitrogen or sulfur [17–19]. Benzothiazole (BNS) and its derivatives are known to be applicable as organic corrosion inhibitors for iron and copper due to the presence of sulfur and nitrogen in their molecular structure [20–23]. The comparison between inhibition properties of benzotriazole and benzothiazole on steel in 1 M hydrochloric acid has been reported [24,25]. However to the best of our knowledge there is no report about the effects of molecular structure of benzotriazole and benzothiazol on the corrosion protection of copper.

Different aspects of corrosion inhibition properties of benzotriazole have been investigated via surface enhanced Raman scattering (SERS) [26], Fourier transform Raman spectroscopy (FTRS) [27], frequency-dependent alternating-current scanning electrochemical microscopy (AC-SEM) [28], IR reflectance spectroscopy [29], polarograph investigations [30], electrochemical frequency modulation (EFM) [25] X-ray photoelectron spectroscopy and impedance studies [31].

Common electrochemical tools, in particular electrochemical impedance spectroscopy (EIS) and DC polarization, have been widely utilized in order to investigate the inhibition performance of various inhibitors for a long period of time. In the recent decade, an

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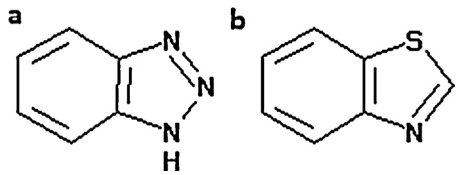

Fig. 1. Chemical structures of (a) benzotriazole (BTA) and (b) benzothiazole (BNS).

increasing interest toward applying new brand techniques such as electrochemical noise method (ECN) have been spotted among corrosion researchers. It has been shown that ECN is a more accurate and powerful technique compared with EIS and DC polarization for studying corrosion properties of metals in inhibitor containing solutions. ECN is traced back to stochastic pulses occurring in the corrosion potential or galvanic current of a freely corroding cell. It is a non-intrusive technique giving both kinetic and mechanistic information [32,33]. Up to now, few investigations have been reported about studying the inhibition properties of the organic inhibitors with electrochemical noise measurement [34–36].

Both BTA and BNS are organic inhibitors based on azoles. They have similar chemical structures but with a slight difference. BTA has three heteroatoms of N but BNS has one N and one S. We have tried to investigate the effects of molecular structure on the corrosion inhibition effects of these azole based derivatives in sulfuric acid solution on copper. The effect of DC trend on the interpretation of electrochemical noise (ECN) results in time domain was evaluated using MAR method. Accordingly, the impact of square and Hanning window functions as drift removal methods in frequency domain was studied. After DC trend removal, it is intended to seek the correlation between ECN data and the results of EIS and LP measurements. To top it off, informative parameters of characteristic charge (q) extracted from the electrochemical noise measurements revealed some good ideas of ongoing phenomena on the surface of Cu immersed in sulfuric acid solution.

2. Experimental

2.1. Materials

It has been aimed to investigate the inhibition effects of benzotriazole (BTA) and benzothiazole (BNS) inhibitors on the corrosion of Cu specimens (having 99% purity, 1 cm^2 area and 1.5 mm thickness) in 1 M H_2SO_4 solution. The inhibitors were purchased from Merck Co. The chemical structures of the inhibitors are given in Fig. 1.

The surface of Cu specimens was carefully abraded by different grades of sand papers ended with the 1000 grade before the measurements. Samples were then washed with water and dried with a filter paper. The corrosive electrolyte was prepared using 1 M sulfuric acid (H_2SO_4) in deionized water. BTA and BNS were added to 1 M H_2SO_4 solution at 100, 200, 400 and 600 ppm.

2.2. Testing methods

2.2.1. ECN and EIS measurements

Different electrochemical techniques including electrochemical impedance spectroscopy (EIS) and electrochemical noise were utilized in order to evaluate the inhibition effects of the inhibitors on the corrosion of copper in 1 M H_2SO_4 solution (naturally aerated solution). In the ECN technique, the electrochemical potential and current noise were measured simultaneously by connecting two coated panels and Ag/AgCl reference electrode to the ECN port of Autolab model PGSTAT302N. The measurement acquisition was performed during a period of 1024 s at 1 s intervals, resulted in a frequency range from close to 1 mHz to 0.5 Hz determined by the expressions $f_{max} = 1/2\Delta t$ and $f_{min} = 1/N\Delta t$ where Δt and N are the sample interval and the total number of data recorded, respectively. The DC trend was removed from measured data before statistical data analysis. The test was carried out in 1 M H_2SO_4 solutions containing different concentrations of BTA and BNS.

The inhibition properties of BTA and BNS on the corrosion of Cu in 1 M H_2SO_4 solution (naturally aerated solution) were also studied by an electrochemical impedance spectroscopy (EIS). The test was carried out by an AUTOLAB PGSTAT302N at perturbation and frequency range of $\pm$10 mV and 10 kHz–100 mHz, respectively. The number of data points per frequency decade in EIS measurement was 7. The electrochemical system included platinum electrode (auxiliary electrode), saturated Ag/AgCl electrode (reference electrode) and metal sheet (working electrode). The test was carried out in one H_2SO_4 solution without and with different concentrations of BTA and BNS.

To obtain impedance data, frequency response analysis (FRA) was used as measuring procedure. In both EIS and ECN techniques, the test was carried out on three replicates to ensure the measurement repeatability.

2.2.2. Potentiodynamic polarization technique

Electrochemical parameters including corrosion current density (I_{corr}), corrosion inhibition efficiency (η) and corrosion rate of samples were obtained from potentiodynamic polarization measurements. The test was carried out by an AUTOLAB PGSTAT302N at scan rate and potential range (with respect to open circuit potential (OCP)) of 1 mV s^{-1} and $\pm$200 mV, respectively. For this purpose, 1 cm^2 area of the samples were exposed to 1 M H_2SO_4 solution containing various concentrations of BTA and BNS. The rest of the Cu surface was masked by a waterproof mixture of 3:1 of beeswax-colophony. The electrochemical system used for this purpose included platinum (auxiliary electrode), saturated Ag/AgCl (reference electrode) and metal sheet (working electrode). The corrosion current density (I_{corr}) was obtained from Tafel extrapolation of polarization curves.

2.2.3. Scanning electron microscope (SEM)

The surface morphology of the Cu samples was studied by a Philips XL30 scanning electron microscope (SEM) before and after exposure to 1 M H_2SO_4 solution in the presence and absence of BNS and BTA inhibitors.

3. Results and discussion

3.1. SEM studies

The surface morphology of the samples exposed to 1 M H_2SO_4 solution was studied by SEM. The SEM micrographs are shown in Fig. 2.

Fig. 2b shows a severe dissolution of Cu in exposure with H_2SO_4 solution without inhibitor. This resulted in the increase of surface porosity together with large and deep holes creation on the metal surface. However, the visual performance of Cu surface exposed to H_2SO_4 solution was significantly changed in the presence of inhibitors. Fig. 2b, c and d shows that dissolution rate of Cu was considerably reduced in the presence of both BTA and BNS inhibitors by formation of a protective film on the metal surface. However, the surface of the sample exposed to H_2SO_4 solution containing BNS is smoother than the one containing BTA. These results could support the higher inhibition efficiency of BNS compared with BTA.

3.2. Potentiodynamic polarization measurements

Potentiodynamic polarization curves of the Cu samples exposed to H_2SO_4 solution with different concentrations of BTA and BNS inhibitors are shown in Fig. 3.