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Investigation of indole-3-carboxylic acid as steel inhibitor in 0.1 M H_2SO_4 solution

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ABSTRACT

Corrosion inhibition of indole-3-carboxylic acid (ICA) on mild steel in 0.1 M H_2SO_4 solution has been studied through weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and scanning electron microscope (SEM) experiments. Plots from polarization and EIS techniques show ICA acts as a mixed type inhibitor and its high inhibition effectiveness is assumed to occur via the adsorption of the inhibitor molecules on steel surface. It is then found that this adsorption behavior obeys the Langmuir adsorption isotherm. Theoretical techniques incorporating molecular mechanics and molecular dynamics were used to simulate the adsorption of ICA molecule on Fe(1 1 0) surface.

Introduction

Mild steel is widely used in many industrial fields due to its valuable mechanical properties and good resistance to corrosion in several media. The chemical cleaning treatments for the process equipments are usually carried out to remove the incrustations and corrosion products. During the chemical cleaning procedure, however, there is the risk that the mild steel may corrode upon the already cleaned steel surface in company with the removal of the corrosion products. This problem leads to not only the loss of the dissolved steel but also the waste in the acid consumption [1]. Therefore, a lot of techniques have been considered to eliminate the destructive effect as much as possible, examples are the adoption of corrosion inhibitor, electrochemical protection, metal and non-metallic coating protective technology [2–5]. The use of inhibitors turns out to be one of the most practical and economical way to restrain metal dissolution and minimize acid consumption. These organic inhibitors will not completely eliminate corrosion, but they are able to reduce the rate at which corrosion occurs, and block early corrosion damage [6–8]. In many cases, thus inhibitors are added into the fluid media so that the inhibitors acts via some adsorption mechanism as they interact with metal surface immersed in solution. As reported, most of the efficient acid inhibitors are organic compounds that contain mainly nitrogen, sulfur or oxygen atoms in their molecular structures [9]. Inhibition of these organic compounds is probably attributed to the interaction between mild steel surface and inhibitor molecules via adsorption. This adsorption behavior is influenced by many factors such as the nature and surface charge of the metal, the chemical structure of the inhibitor molecule, the type of aggressive medium, and the temperature of the corrosion reaction. Chemisorption and physisorption are two basic types of interaction responsible for bonding of inhibitor to metal surface.

Commonly, the organic inhibitor molecules can replace the water molecules absorbed onto the metal surface and block the anodic and/or cathodic reaction sites to retard the oxidation and/or reduction corrosion reaction. To our best understanding, the inhibition efficiency of organic compounds depends on the molecular structure of inhibitor, the characteristics of the environment, and the mode of interaction with the metal surface [10]. Indole and some derivates of indole have been tested as corrosion inhibitors in acid solutions, and the experimental results show very good inhibition performance for metal corrosion in different aggressive electrolyte [11–13]. The present work aims at investigating the inhibitive action of indole-3-carboxylic acid (ICA) on mild steel in 0.1 M H_2SO_4 solution using electrochemical,

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weight loss, and theoretical techniques. Specially, the weight loss measurements are performed at the temperature range of 298–318 K. As a consequence, the thermodynamic and kinetic parameters are discussed, and the theoretical calculations provide us a better understanding of the interaction mechanism between the inhibitor molecule and the iron surface. Fig. 1 demonstrates the molecular structure of ICA.

Experimental part

Materials and sample preparation

The tested inhibitor, namely, indole-3-carboxylic acid (ICA) was purchased from Aladdin® with the purity of 99% and dissolved in 0.1 M H_2SO_4 at various concentrations (from 1×10^{-3} to 4×10^{-3} M). The electrolyte 0.1 M H_2SO_4 was prepared from analytical reagent grade 97% H_2SO_4 and distilled water. The composition (wt%) of the mild steel used in experimental was: Fe 99.15, 0.16 C, 0.43 Mn, 0.24 Si, 0.015 S, and 0.0049 P. Mild steel sheet with dimension of $40.0 \times 30.0 \times 2.0$ cm^3 was mechanically cut into different sizes with dimensions of $4.0 \times 3.0 \times 2.0$ cm^3 and $1.0 \times 1.0 \times 1.0$ cm^3, which are used for weight loss and SEM measurements, respectively. The surfaces of all the specimens were polished successively using SiC paper up to grade 1200, degreased with acetone, rinsed with distilled water, dried at room temperature, and finally placed in desiccator.

Weight loss experiments

To evaluate the adsorption characteristics and the activation parameters of corrosion process, weight loss tests were conducted at 298, 308, and 318 K, in the absence and presence of inhibitor at various concentrations during 24 h of immersion. The initial weight of the specimen was recorded using an analytical balance (accuracy $\pm$ 0.1 mg). The surface area of every specimen was also calculated accurately before the immersion. After the immersion, the specimens were cleaned using a bristle brush in distilled water and acetone, respectively. Then the specimens were subjected to ultrasonic cleaning for 3 min. Finally dried at room temperature and reweighed. The mean value of corrosion rate (CR) was determined through parallel experiments under the same condition.

Electrochemical experiments

In electrochemical tests, the specimens were imbedded in epoxy resin with a surface area of 1.00 cm^2 exposed to the corrosive medium. Electrochemical tests were performed in a traditional three electrode glass cell filled with 250 ml of acid solution in the absence and presence of various concentrations of inhibitor. The temperature was thermostatically controlled at 298 K using an aqueous thermostat. Platinum with 2.0 cm $\times$ 2.0 cm dimension was used as counter electrode. Saturated calomel electrode (SCE) provided with a Luggin capillary probe was taken as a reference electrode. At the beginning of the corrosion test, the working electrode was allowed to corrode freely for 50 min to reach a quasi-stationary state for the open circuit potential (OCP). This steady-state OCP corresponds to the corrosion potential of the working electrode.

Electrochemical impedance measurements were carried out at a current frequency range that extended from 10^{-2} Hz to 10^5 Hz at the corrosion potential. The amplitude of the oscillation was $\pm$5 mV. Anodic and cathodic polarization curves, in the presence and in the absence of ICA, were obtained staring from the cathodic potential of $-$0.250 V to an anodic potential of +0.250 V versus the corrosion potential. The effects of scan rate on the potentiodynamic polarization curve obtained to determine the Tafel slopes and corrosion current density are significant (see more details in Ref. [14]). Thus, a low scan rate (0.5 mV s^{-1}) was used to minimize the disturbance of the charging current.

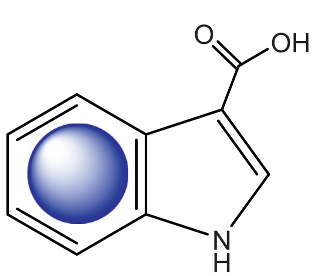

Fig. 1. Molecular structure of the studied inhibitor ICA.

SEM analysis

The surface morphologies of mild steel specimens after immersion in uninhibited and inhibited acid solutions for 12 h were evaluated using a scanning electronic microscope (KYKY2800B). The accelerating voltage was 25 kV.

Theoretical calculations

Theoretical studies were performed to examine the reaction activity of ICA molecule, and clarify the interaction between interested inhibitor and the iron surface. The quantum chemical calculations were performed using Gaussian 09 program package [15]. The molecular geometry was optimized using DFT methods at the B3LYP/6-311 + + G(d,p) level [16]. The frequency calculations were employed to confirm the structures as minimum points in energy and achieve the relevant zero point energy. Besides, the interaction between a single ICA molecule and the iron surface was investigated by performing Monte Carlo simulations using the adsorption locator module. The calculations were carried out, using the COMPASS force field [17], in a simulation box (12.4 Å $\times$ 12.4 Å $\times$ 33.1 Å) with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. A cutoff distance of 1.55 nm with a spline switching function was applied for the non-bond interactions. A low-energy adsorption site is identified by carrying out a Monte Carlo search of the configurational space of the substrate–adsorbate system as the temperature is slowly decreased [18]. This process is repeated to identify further local energy minima. During the course of the simulation, adsorbate molecules are randomly rotated and translated around the substrate. The configuration that results from one of these steps is accepted or rejected according to the selection rules of the Metropolis Monte Carlo method [19].

Results and discussion

Weight loss experiments

Fig. 2 shows the effect of inhibitor concentration and temperature on the corrosion rate and inhibition efficiency. The detailed corrosion parameters from weight loss tests in 0.1 M H_2SO_4 solution containing various concentrations of ICA are summarized in Table 1. Corrosion rate (v), inhibition efficiency (IE%), and surface coverage (θ) are calculated as following formulas, respectively:

$$v = \frac{\Delta W}{St} \tag{1}$$