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Investigation of corrosion inhibition of carbon steel in 0.5 M H_2SO_4 by new bipyrazole derivative using experimental and theoretical approaches

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ABSTRACT

2-[Bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-4-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl) carbamoyl]-butyric acid (Pyr1-1) has been evaluated as a corrosion inhibitor for carbon steel using weight loss and electrochemical polarization (EIS). The study was also complemented by scanning electron microscopy (SEM) and quantum chemical calculations. The inhibition efficiency (η%) increased with increasing Pyr1-1 concentration, showing a maximum IE of 93.5% at 298 K at 10^{-3} M and decreased with increasing temperature. The electrochemical studies showed that Pyr1-1 inhibitor retards both cathodic and anodic processes through the inhibitor adsorption on the metal surface and blocking the active corrosion sites. The corrosion current density is the order 165.8 μA/cm^2 of Pyr1-1 at the optimum concentration. EIS results show that the change in the impedance parameters (R_{ct} and C_{dl}) with concentration of Pyr1-1 is indicative of the adsorption of molecules leading to the formation of a protective layer on the surface of carbon steel. A good fit to Langmuir adsorption isotherm was obtained between surface coverage degree and inhibitor concentration. The results obtained by weight loss measurements are consistent with the results of the electrochemical study. Quantum chemical approach used to calculate electronic properties of the molecule to ascertain the relation between inhibitive effect and molecular structure. The equilibrium adsorption behavior of this molecule on Fe (1 1 0) surface was investigated using molecular dynamics simulation.

1. Introduction

The corrosion of materials is one of the main problems faced by industrial processes, generating huge financial losses. Metallic industrial structures are often exposed to conditions that facilitate corrosive processes. For example, acidic solutions, which are widely used in acid pickling, industrial acid cleaning and oil refinery equipment cleaning, promote the acceleration of metallic corrosion, affecting the performance and durability of the treated equipment [1,2].

The use of organic inhibitors for preventing corrosion is a promising alternative solution. These inhibitors are usually adsorbed on the metal surface by the formation of a coordinate covalent bond (chemical adsorption) or the electrostatic interaction between the metal and inhibitor (physical adsorption) [3]. This adsorption produces a uniform film on the metal surface, which reduces or prevents contact with the corrosive medium [4].

Most of the effective organic inhibitors used contain heteroatoms such as O, N, S and multiple bonds in their molecules through which they are adsorbed on the metal surface [5–9]. It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor group, such as functional groups, electron density at the donor atom, π-orbital character, and the electronic structure of the molecule [10]. One technique that has been used to evaluate organic corrosion inhibitors is molecular modeling. Through quantum chemical calculations, it is possible to obtain structural parameters, such as the energies of the frontier molecular orbitals, the HOMO (highest occupied

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molecular orbital) and LUMO (lowest unoccupied molecular orbital), and the dipole moment. These parameters influence the potential inhibition and are generally strongly correlated with the experimentally obtained inhibition efficiency [11–16]. Thus, this technique is an important tool for pre-selecting possible corrosion inhibitors and studying the correlation between molecular structure and corrosion inhibition efficiency [17].

Accordingly, the aim of this work is to study the inhibition action of 2-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-4-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-carbamoyl]-butyric acid (Pyr1-1), on the corrosion of carbon steel in sulfuric acid. The inhibition performance is evaluated by weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements, complemented with scanning electron microscopy and quantum calculations. The chemical structure of the studied 2-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-4-[bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-carbamoyl]-butyric acid (Pyr1-1) is given in Fig. 1.

2. Experimental methods

2.1. Materials

The steel used in this study is a carbon steel (CS) (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370% C, 0.230% Si, 0.680% Mn, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% Cu and the rest being iron (Fe).

2.2. Solutions

The aggressive solutions of 0.5 M H_2SO_4 was prepared by dilution of analytical grade 98% H_2SO_4 with distilled water. The concentration range of (Pyr1-1) employed was 10^{-6}–10^{-3} M.

2.3. Inhibitor

In the studied, the tridentate compound presented in Fig. 1, which is tested as a corrosion inhibitor was synthesized according to our used and known experimental methods [18–20]. The compound has been prepared by condensation of one equivalent of the (3,5-dimethyl-pyrazol-1-yl)-methanol and one equivalent of the 2-amino-pentanedioic acid in acetonitrile as solvent, by stirring for 4 days at room temperature. The product has been purified and characterized by ^{1}H NMR, ^{13}C NMR spectroscopy and mass spectroscopy analysis.

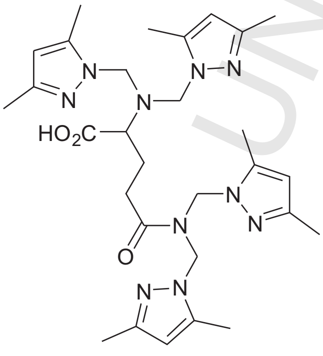

Fig. 1. The chemical structure of the studied bipyrazolic compound.

2.4. Measurements

2.4.1. Weight loss measurements

Gravimetric experiments were performed according to the standard methods [21], the carbon steel (CS) sheets of 2.0 × 1.0 × 0.3 cm were abraded with a series of emery papers SiC (180, 600, 800, 1000 and 1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in a 100 mL beaker containing 80 mL 0.5 M H_2SO_4 solution with and without addition of different concentrations of Pyr1-1. All the aggressive acid solutions were open to air. After 6 h the steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighted. In order to get good reproducibility experiments were carried out in triplicate. The average weight loss of three parallel CS sheets was obtained. The tests were repeated at 298 K. The corrosion rate (ν) and the inhibition efficiency (η_{WL}) were calculated by the following equations [22]:

$$\nu = \frac{W}{St} \times 100 \qquad (1)$$

$$\eta_{WL}\ (\%) = \frac{\nu_0 - \nu}{\nu_0} \times 100 \qquad (2)$$

where W is the three-experiment average weight loss of the carbon steel, S is the total surface area of the specimen, t is the immersion time and ν_0 and ν are values of the corrosion rate without and with addition of the inhibitor, respectively.

2.4.2. Electrochemical impedance spectroscopy

The electrochemical measurements were carried out using a Volta laboratory (Tacussel-Radiometer PGZ 100) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as an auxiliary electrode of surface area 1 cm^2. The working electrode was carbon steel with the surface area of 1 cm^2. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 min to establish a steady state open circuit potential (*E*ocp). After measuring the *E*ocp, the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 298 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the *x*-axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation [23]:

$$\eta_z\% = \frac{R_{ct}^{i} - R_{ct}^{o}}{R_{ct}^{i}} \times 100 \qquad (3)$$

where, R_{ct}^{o} and R_{ct}^{i} are the charge transfer resistance in absence and in presence of inhibitor, respectively.

2.4.3. Potentiodynamic polarization

The electrochemical behavior of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 0.5 M H_2SO_4 solution containing

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