Inhibitive properties, adsorption and theoretical study of 3,7-dimethyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one as efficient corrosion inhibitor for carbon steel in hydrochloric acid solution

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ABSTRACT

The corrosion inhibition efficiency of 3,7-dimethyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (DPQO) on carbon steel in 1.0 M HCl solution has been investigated using, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), weight loss, and scanning electron microscopy (SEM) methods. The results showed that the inhibition efficiency of DPQO increased with the inhibitor concentration but decreased with temperature. Polarization studies revealed that DPQO acts as a mixed-type inhibitor at 308 K. The inhibitor adsorption on the steel surface obeyed the Langmiur isotherm and the thermodynamic parameters (K_{ads}, ΔG^o_{ads}) were calculated and discussed. The corrosion process in 1.0 M HCl in the absence and presence of DPQO followed first-order kinetics. Activation parameters of the corrosion process (E_a, ΔH_a and ΔS_a) were also calculated from the corrosion rates. SEM results supported the adsorption conclusions. Quantum chemical calculations have been performed using DFT and several quantum chemical indices of DPQO were calculated and correlated with its inhibitive effect.

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1. Introduction

Corrosion prevention is of great importance in industrial application of materials. Among numerous corrosion prevention measures, corrosion inhibitors, bearing advantages of economy, high efficiency, and wide applicability, have been applied in various fields such as petroleum extraction and refining, iron and steel, electric power, construction, etc. [1]. In recent years, with the recognition of environmental protection, development of more effective and environmentally friendly corrosion inhibitors has drawn more attention [2–4]. Most of the efficient inhibitors used in industry are organic compounds which mainly contain oxygen, sulfur, and nitrogen atoms and multiple bonds in the molecule through which they are adsorbed onto the metal surface [5–11]. Moreover, many *N*-heterocyclic compounds have been used as effective inhibitors of corrosion of metals and alloys in aqueous media [12,13]. It has been reported that many organic inhibitors usually promote the formation of a chelate on the metal surface, which includes the transfer of electrons from the organic compounds to the metal, forming coordinate covalent bonding during such chemical adsorption process [14]. In this

way, the metal acts as an electrophile, whereas the nucleophile centers of the inhibitor molecule are normally heteroatoms with free electron pairs which are readily available for sharing, to form a bond.

Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations, which have been proved to be a very powerful tool for studying the mechanism [15,16]. Quantum chemical studies using density functional theory (DFT) have been successfully performed by our research group to link the corrosion inhibition efficiency with the molecular/electronic properties of organic molecules to explain the electron transfer mechanism between the inhibitor and the steel surface [17–19].

The quinoxalines are the heterocycles that frequently found in compounds propertied diverse biological activities [20–23]. The last two decades, literature has brought a large number of work on the biological activity of derivatives quinoxalines. It proved that these derivatives have the activities in various domains: antidiabetic [24], *anti*-HIV agents [25], or anti-tumor agents [26]. In addition, several studies have already carried on the corrosion inhibition of steel in acid medium with organic compounds of type of «quinoxalines» [27–38], have given very good results, which pushed us to seek other new derivatives for testing their inhibitory effects on carbon steel in 1.0 HCl medium.

The present work deals with the corrosion inhibition nature of 3,7-dimethyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (DPQO) in the

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acid medium utilizing; the polarization and electrochemical impedance spectroscopy (EIS) methods and weight loss measurements. The effect of temperature on the corrosion rate was discussed. Both kinetic and standard thermodynamic parameters are calculated and discussed in detail. Quantum chemical calculations have been performed to evaluate several quantum chemical indices and correlated with the corrosion inhibition nature of the inhibitor in 1.0 M HCl medium.

2. Experimental

2.1. Materials

The tested inhibitors, namely 3,7-dimethyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (DPQO) was synthesized according to a previously described experimental procedure [39]. The molecular structure of the DPQO is shown in Fig. 1.

The steel used in this study is a carbon steel (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 remainder iron (Fe).

The aggressive solutions of 1.0 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. The concentration range of 3,7-dimethyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (DPQO) used was 10^{-6} M to 10^{-3} M.

2.2. Electrochemical measurements

The electrochemical measurements were carried out using Volta lab (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 auxiliary electrode of surface area of 1 cm². The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 min to a establish 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 308 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 impedance data were analysed and fitted with the simulation ZView 2.80, equivalent circuit software.

After ac impedance test, the potentiodynamic polarization measurements of carbon steel substrate in inhibited and uninhibited solution were scanned from cathodic to the anodic direction, $E = E_{corr} \pm 200$ mV, with a scan rate of 1 mV s^{-1}. The potentiodynamic data were analysed using the polarization VoltaMaster 4 software. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). From the polarization curves obtained, the corrosion current (I_{corr}) was calculated by curve fitting using the equation:

$$I = I_{corr}\left[\exp\left(\frac{2.3\Delta E}{\beta_a}\right) - \exp\left(\frac{2.3\Delta E}{\beta_c}\right)\right] \tag{1}$$

The inhibition efficiency was evaluated from the measured I_{corr} values using the following relationship:

$$\eta_{Tafel}(\%) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \tag{2}$$

where I_{corr} and $I_{corr(i)}$ are the corrosion current densities for steel electrode in the uninhibited and inhibited solutions, respectively.

2.3. Weight loss measurements

Gravimetric experiments were performed according to the standard methods [40], the carbon steel sheets of $1.6 \times 1.6 \times 0.07$ cm were abraded with a series of emery papers SiC (120, 600 and 1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in a 50 mL beaker containing 80 mL of 1.0 M HCl solution with and without addition of different concentrations of DPQO. All the aggressive acid solutions were open to air. After 6 h of acid immersion, the specimens were taken out, washed, dried, and weighed accurately. In order to get good reproducibility, the experiments were carried out in triplicate in each case and the mean value of the weight loss is calculated.

2.4. Scanning electron microscopy (SEM)

The morphology of state surface was performed using a JEOL JSM-5800 Scanning Electron Microscopy. The energy of the acceleration beam employed was 20 kV. The analysis by SEM was carried out on the surface of carbon steel samples before and after immersion in the acidic solutions with and without the optimal concentration of DPQO inhibitor.

2.5. Quantum chemical calculations

Density Functional theory (DFT) has been recently used [41–44], to describe the interaction between the inhibitor molecule and the surface as well as the properties of these inhibitors concerning their reactivity. The molecular band gap was computed as the first vertical electronic excitation energy from the ground state using the time-dependent density functional theory (TD-DFT) approach as implemented in Gaussian 03 [45]. For these seek, some molecular descriptors, such as HOMO and LUMO energy values, frontier orbital energy gap, molecular dipole moment, electronegativity (χ), global hardness (η), softness (σ), the fraction of electron transferred (ΔN), were calculated using the DFT method and have been used to understand the properties and activity of the newly prepared compounds and to help in the explanation of the experimental data obtained for the corrosion process.

According to Koopman's theorem [46], the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations.
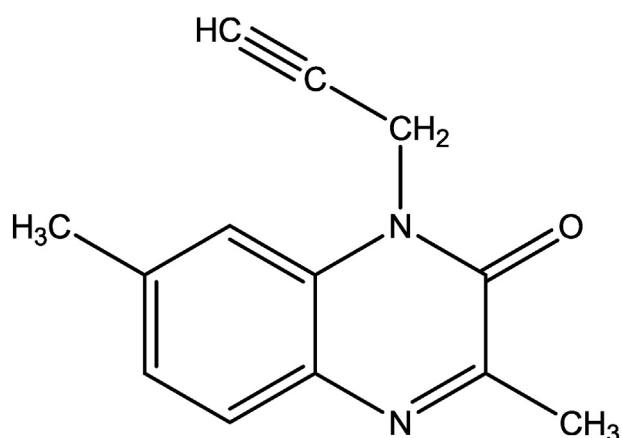
$$IE = -E_{HOMO} \tag{3}$$

Fig. 1. Chemical structure of 3,7-dimethyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (DPQO).

$$EA = -E_{LUMO} \tag{4}$$