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Synthesis, characterization and the inhibition activity of a new α-aminophosphonic derivative on the corrosion of XC48 carbon steel in 0.5 M H_2SO_4: Experimental and theoretical studies

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ABSTRACT

A new aminophosphonic derivative was synthesized and characterized by UV-vis, IR, ^{1}H NMR, ^{13}C NMR and MS spectroscopic methods. Its inhibitive action on the carbon steel corrosion in a 0.5 M H_2SO_4 solution was studied by polarization curves and electrochemical impedance spectroscopy (EIS). The results indicated that the synthesized compound is an efficient mixed-type inhibitor and its inhibition efficiency increased with increasing the inhibitor concentration. The adsorption of the inhibitor on the carbon steel surface obeys Langmuir isotherm and the thermodynamic parameters were obtained. The surfaces of carbon steel after exposing to test solutions were examined by atomic force microscopy (AFM). The quantum chemical parameters were calculated in gas and aqueous phases using the density functional method (DFT). The interaction between the inhibitor and Fe (100) surface were performed by molecular dynamic simulations.

1. Introduction

Corrosion is one of the most common problems raised in our daily life and in various industrial fields, such as the petrochemical industry, machine and instrument industries, hydrocarbons transport and water treatment plants. The use of organic inhibitors in various corrosive media, especially in acidic media, is an effective way to protect metals against corrosion [1]. The inhibition effect depends on many factors including the molecular structure, the physicochemical and the electronic properties of the inhibitor. These factors are related to the functional groups present in the inhibitor, steric effects, the electronic density of donor atoms, and orbital character of the donating electrons [2,3]. Generally, the adsorption of organic inhibitors on a metal surface forms complexes layer with the metal atoms, protecting hence the metal from corrosion [4–6]. Organic inhibitors containing triple or conjugated double bonds, or aromatic rings in their molecular structures, and those rich in heteroatoms such as sulfur, phosphorus, nitrogen and oxygen were found to have higher electronegativity and electron donating ability; which increase the inhibition efficiency of these compounds in acid media [7–9]. Several studies investigating the implementation of phosphonates, α-amino-phosphonates and their derivatives as corrosion inhibitors have been carried out for iron or steel in a wide range of corrosive media [10–13]. Those compounds were essentially selected based on the empirical knowledge of their macroscopic physicochemical properties. As the phosphonates and α-aminophosphonates derivatives are nontoxic and biodegradable, studying their inhibiting properties would be significant in the context of the current priority to produce eco-friendly inhibitors. Owing to the fact that using those compounds at the usual concentrations for corrosion inhibition has a negligible impact on the environment [14,15]. Various synthetic methods for phosphonates, α-aminophosphonates and α-aminophosphonic acids have been reported. Among them, the most remarkable ones for phosphonates and α-aminophosphonates is the Michaelis Arbuzov and Kabachnik-Fields reactions [16–22].

Recently, computational chemistry methods were widely employed to study organic compounds as corrosion inhibitors, and

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also to determine the relationship between the molecular structure of these compounds and their inhibition efficiency [23–26]. In this context, the electronic properties relevant to the inhibiting action were calculated. Furthermore, molecular dynamic simulations are largely used to elucidate the adsorption of the inhibitor on the metal surface at a molecular level [27,28]. These simulations give an interpretation of the adsorption mode of the inhibitor molecule on the metal surface and allows to obtain the value of the adsorption energy between the organic inhibitor and metal surface.

In the present work, a new α-aminophosphonic derivative was synthesized and its structure was confirmed by different spectroscopic methods including: UV-vis, FTIR, ^{1}H NMR, ^{13}C NMR and MS. The inhibition effect of the synthesized derivative on the corrosion of carbon steel in a 0.5 M H_2SO_4 solution was investigated using potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. The adsorption isotherm of the inhibitor on carbon steel surface and the standard adsorption free energy (ΔG^0_{ads}) were obtained. The quantum chemical parameters such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE_{GAP}), dipole momentum (μ), Mulliken charges, hardness (η), softness (σ), and molecular electrostatic potential map (ESP) of the neutral and protonated inhibitor were calculated in gas and aqueous phases. Molecular dynamic simulations were performed in a vacuum slab and aqueous solutions using the adsorption locator module to obtain adsorption configurations and energies of the α-aminophosphonic derivative on the Fe (100) surface.

2. Experimental

2.1. Materials

All corrosion tests were performed with XC48 carbon steel specimens with the following chemical composition (wt.%): C = 0418%, Mn = 0730%, Mo = 0012%, P = 0016%, S = 0019%, Si = 0245%, Ni = 0079%, F = 0777% and Fe = 98,0,9873%. The mild steel working electrode surfaces were successively cleaned with SiC abrasive papers (600, 800, 1000, 1200 and 1800 grades), washed with bidistilled water and finally degreased with acetone and dried at room temperature.

2.2. Solutions

The aggressive 0.5 M H_2SO_4 solution electrolyte was prepared by the dilution of a Sigma-Aldrich analytical grade 98% H_2SO_4 with bidistilled water. The inhibitor concentration was varied from 10^{-5} to 10^{-3} M.

2.3. Synthesis of the corrosion inhibitor

The studied α-aminophosphonic derivative; namely 4-(2-{[*ethoxy*(*hydroxy*)*phosphonyl*](3-nitrophenyl)methyl}hydrazinyl)benzoic acid, was synthesized by the reaction between 3-nitrobenzaldehyde (1.0 mmol), 4-hydrazinylbenzoic acid (1.0 mmol), and diethylphosphite (1.2 mmol) respectively in $FeCl_3$.THF (3 mL, 5.0%) solution for an appropriate reaction time at reflux temperature until the formation of the precipitate. which was then filtered, washed with petroleum ether and dried at room temperature. The synthesis procedure of the studied α-aminophosphonic compound is shown in Fig. 1. The main characteristics of the synthesized derivative are the following:

Yield: 78% of yellow solid; UV–Vis (DMSO): $\lambda_{max(n)}$ (nm),: $\lambda_{max(1)}$ (221); $\lambda_{max(2)}$ (276); $\lambda_{max(2)}$ (360). IR (Solid state) ν_x (cm^{-1}): 3454, 3264, 3121, 2853, 2925, 2585, 2360, 1689, 1272, 958, 762, 729. ^{1}H NMR (400 MHz, DMSO-d6), δ (ppm), (Fig. 2a): 11.149 (s, 1H, C–OO**H**), 08.491 (s, 1H, P–O**H**), 8.162 (m, 2H, C**H$_{ar}$**), 8.081 (m, 2H, C**H$_{ar}$**), 7.876 (m, 2H, C**H$_{ar}$**), 7.706 (m, 2H, C**H$_{ar}$**), 7.200 (s, 1H, N**H**), 7.179 (s, 1H, N**H**), 4.271 (m, 2H,C**H$_2$**), 3.802 (s, 1H,C**H**), 1.310 (m, 3H, C**H$_3$**). ^{13}C NMR (400 MHz, DMSO-d6), δ (ppm), (Fig. 2b): 166.583, 166.131, 149.081, 148.804, 137.675, 137.194, 132.411, 131.504, 130.687, 123.163, 120.593, 112.136, 60.456, 52.014, and 14.802. MS (m/z, %), (Fig. 3): 397 (M+2, 3.7), 396 (M+1, 19.43), 395 ($M^{+\bullet}$, 100), 394 (M−1, 9.7), 378 (8.1), 366 (45.2), 350 (27.60), 349 (26.3), 286 (68.4), 274 (17.1), 273 (39), 259 (10.4), 244 (8.1), 151 (29.3), 136.5 (5.3), 122.5 (9.8), 121 (9.4), 109.5 (31.12), 46 (4.6), 45 (3.4), 29 (8.1), 17 (12.1).

2.4. Electrochemical measurements

A conventional three-electrode thermostated cell was used for the electrochemical experiments with carbon as the counter electrode (CE), a saturated calomel electrode (SCE) as the reference electrode (RE) and a XC48 carbon steel as the working electrode (WE). All the potentiodynamic curves were performed using a PGZ 310 Voltalab40 computer fitted (potentiostat/galvanostat) system and the obtained data were plotted and analyzed using Voltamaster 4 software.

Before starting any electrochemical measurement, the working electrode was immersed in the experimental solution for 60 min at room temperature (20 ± 1 °C) under an open circuit potential (E_{OCP}) to reach a stable steady state. The Tafel potentiodynamic polarization curves were obtained by automatically varying the potential from −800 to −200 (mV/SCE) with a scan rate of 0.5 mV s^{-1}. The following equation was used to determine the inhibition efficiency obtained from the polarization curves (E_p %) [29]:

$$E_p\% = \frac{i^{\circ}_{corr} - i_{corr(inh)}}{i^{\circ}_{corr}} \times 100 \quad (1)$$

where i°_{corr} and $i_{corr(inh)}$ represents the corrosion current density values in the absence and presence of inhibitor respectively.

The values of the surface coverage (θ) were calculated using the following equation:

$$\theta = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \quad (2)$$

Electrochemical impedance (EIS) measurements were carried out at open circuit potential in the frequency range of 100 kHz to 10 mHz, with an amplitude signal perturbation of 5 mV. The Inhibition efficiency obtained from the electrochemical impedance spectroscopy (E_R %) was calculated using the following equation [29] :

$$E_R\% = \frac{R_{t(inh)} - R_{t(0)}}{R_{t(inh)}} \times 100 \quad (3)$$

where $R_{t(0)}$ and $R_{t(inh)}$ are the charge transfer resistance values in the absence and presence of the inhibitor, respectively.

2.5. Surface characterization

The surface morphology of the polished carbon steel before and after 24 h of immersion in 0.5 M H_2SO_4 in the absence and presence of the inhibitor at 20 °C was investigated using the Atomic Force Microscopy AFM using an Asylum Research MFP-3D Classic AFM instrument.

3. Computational details

3.1. Quantum chemical calculations

All quantum chemical calculations and visualization of the results were performed using the standard GAUSSIAN 09 W program package [30] and GaussView 5.0.8 software [31]. The geometry of