Progress in Organic Coatings 67 (2010) 420–426

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Short communication

Adsorption and inhibition effect of vanillin on cold rolled steel in 3.0 M H_3PO_4

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ARTICLE INFO

Article history:
Received 5 August 2009
Received in revised form
11 December 2009
Accepted 16 December 2009

Keywords:
Cold rolled steel
Vanillin
Corrosion inhibitor
AFM
Adsorption
Quantum chemical calculation

ABSTRACT

The adsorption and inhibition effect of vanillin (4-hydroxy-3-methoxy-benzaldehyde) on cold rolled steel (CRS) in 3.0 M H_3PO_4 at 30–60 °C was investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The results show that inhibition efficiency increases with the inhibitor concentration, while decreases with temperature. The adsorption of vanillin obeys Temkin adsorption isotherm. The thermodynamic parameters (adsorption enthalpy ΔH_{ads}, adsorption free energy ΔG_{ads} and adsorption entropy ΔS_{ads}) have been calculated and discussed in detail. Polarization curves show that vanillin acts as a mixed-type inhibitor. EIS shows that charge transfer resistance increases while the capacitance of double layer decreases with the inhibitor concentration, confirming the adsorption process mechanism. The adsorbed film on CRS surface containing vanillin was examined by atomic force microscope (AFM). Quantum chemical calculation was applied to elucidate the adsorption mode of the inhibitor molecule onto steel surface. Depending on the results, the inhibitive mechanism is proposed from the viewpoint of adsorption theory.

1. Introduction

The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [1]. Most well known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms. It is generally accepted that organic molecules inhibit corrosion by adsorption on metal surface. Furthermore, the adsorption depends on the molecule's chemical composition, temperature and electrochemical potential at the metal/solution interface. So the study of relationship between the adsorption and corrosion inhibition is of great importance. Though many organic compounds show good anticorrosive activity, most of them are highly toxic. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system, namely, kidneys or liver, or to disturb a biochemical process or to disturb an enzyme system at some site in the body [2]. The investigation of new non-toxic or low-toxic and green corrosion inhibitors is essential to overcome this problem. In the 21st Century, the research in the field of "green" or "eco-friendly" corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules at low or "zero" environmental impact. In recent days many alternative eco-friendly organic inhibitors including amino acids [3–5], aromatic aldehydes [6], polymers [7], phytic acid [8], etc. were studied.

Phosphoric acid (H_3PO_4) is widely used in the surface treatment of steel such as chemical and electrolytic polishing, chemical coloring, chemical and electrolytic etching, removal of oxide film, phosphating, passivating, and surface cleaning. However, phosphoric acid shows strong corrosiveness on ferrous and ferrous alloys. Accordingly, there is a great need to protect steel in the phosphoric acid medium. Up to now, little work [7,9–11] appears to have been done on the inhibition of steel in H_3PO_4 solution.

Vanillin (4-hydroxy-3-methoxy-benzaldehyde) is one of the most widely used and important flavoring materials worldwide. It has many advantages such as low cost, non-toxicity and easy production. The annual production capability in the world can reach to 12,000 ton [9]. This makes the investigation of vanillin inhibiting properties significant. In 2001, El-Etre [10] investigated the effect of vanillin on the corrosion of aluminum in 5.0 M HCl. The results show that inhibition efficiency (IE) is 98% at 2000 mg/L, and its adsorption obeys Langmuir adsorption isotherm. Afterwards, Emergül and Hayvalı [11] studied the corrosion inhibition of vanillin on steel in 2.0 M HCl, and the inhibition efficiency is about 85% with 0.01 M (about 1512.5 mg/L) inhibitor. Its adsorption also follows Langmuir adsorption isotherm. However, the literature available to date about effect of vanillin on the corrosion of steel in H_3PO_4 solution is very scarce.

In order to extend vanillin as corrosion inhibitors, this paper focus on the corrosion inhibition by vanillin for steel in 3.0 M H_3PO_4. Weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods were employed to evaluate corrosion rate of steel and inhibition efficiency of the

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doi:10.1016/j.porgcoat.2009.12.006

inhibitor. Meanwhile, the steel surface was examined by atomic force microscope (AFM). In addition, the adsorption isotherm of vanillin on CRS surface is obtained. Thermodynamic parameters (adsorption heat ΔH^0, adsorption free energy ΔG^0 and adsorption entropy ΔS^0) are calculated and discussed in detail. It is expected to provide useful information on the adsorption and inhibition effect of vanillin on steel in phosphoric acid solution.

2. Experimental method

2.1. Materials

Tests were performed on cold rolled steel (CRS) of the following composition (wt.%): 0.07% C, 0.3% Mn, 0.022% P, 0.010% S, 0.01% Si, 0.030% Al, and bal. Fe.

2.2. Inhibitor

Vanillin was obtained from Shanghai Chemical Reagent Company of China, and of analytical-reagent (AR) grade. Fig. 1 shows the molecular structure of vanillin.

2.3. Solutions

The aggressive solutions, 3.0 M H_3PO_4 were prepared by dilution of analytical grade 85% H_3PO_4 with distilled water. The concentration range of vanillin was 25–500 mg/L (1.64×10^{-4}–3.29×10^{-3} M).

2.4. Weight loss measurements

The cold rolled steel (CRS) sheets of 2.5 cm × 2.0 cm × 0.06 cm were abraded with a series of emery paper (grade 320-500-800) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in 250 mL beaker, which contained 250 mL 3.0 M H_3PO_4 with and without different concentrations of vanillin. All the aggressive acid solutions were open to air. After immersion for 6 h, the specimens were taken out, washed, dried, and weighed accurately. The average weight loss of three parallel CRS sheets was obtained. Then the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in triplicate. In the present study, the standard deviation values among parallel triplicate experiments were found to be smaller than 5%, indicating good reproducibility. The corrosion rate (v) was calculated from the following equation [12]:

$$v = \frac{W}{St} \quad (1)$$

where W is the average weight loss of three parallel CRS sheets, S the total area of one CRS specimen, and t is the immersion time (6 h). With the calculated corrosion rate, the inhibition efficiency (IE_w) was calculated as follows [12]:

$$IE_w\ (\%) = \frac{v_0 - v}{v_0} \times 100 \quad (2)$$

where v_0 and v are the values of the corrosion rate without and with addition of the inhibitor, respectively.

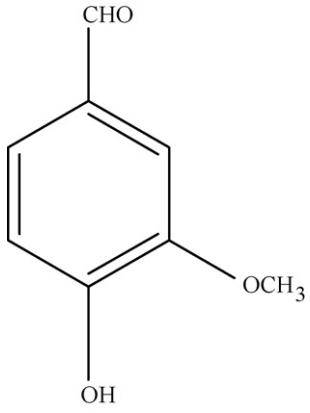

Fig. 1. Chemical molecular structure of vanillin.

2.5. Electrochemical measurements

Electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. To minimize the ohmic contribution, the Luggin capillary was close to working electrode (WE). The WE was in the form of a square CRS embedded in PVC holder using epoxy resin so that the flat surface was the only surface in the electrode. The working surface area was 1.0 cm × 1.0 cm, abraded with emery paper (grade 320-500-800) on the test face, rinsed with distilled water, degreased with acetone, and dried with a cold air stream. Before measurement the electrode was immersed in test solution at open circuit potential (OCP) for 2 h until a steady state was reached. All electrochemical measurements were carried out by PARSTAT 2273 advanced electrochemical system (Princeton Applied Research). Each experiment was repeated at least three times to check the reproducibility.

The potential of potentiodyamic polarization curves was increased at 30 mV/min and started from a potential of −250 mV to +250 mV vs. free corrosion potential (E_{corr} vs. SCE). This measurement was done after the steady state. IE_p (%) was defined as:

$$IE_p\ (\%) = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \quad (3)$$

where I_{corr} and $I_{corr(inh)}$ represent the corrosion current density values without and with inhibitor at the free corrosion potential, respectively.

Electrochemical impedance spectroscopy (EIS) was carried out at OCP in the frequency range of 0.1 Hz–100 kHz using a 10 mV peak-to-peak voltage excitation. IE_{Rt} (%) was determined by the following equation:

$$IE_{Rt}\ (\%) = \frac{R_{t(inh)} - R_{t(0)}}{R_{t(inh)}} \times 100 \quad (4)$$

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

2.6. Atomic force microscope (AFM)

The CRS specimens of size 1.5 cm × 1.0 cm × 0.06 cm were prepared as described above (Section 2.4). After immersion in 3.0 M H_3PO_4 without and with 500 mg/L vanillin at 30 °C for 6 h, the specimens were cleaned with distilled water, dried with a cold air blaster, and then used for a Japan instrument model SPA-400 SPM Unit atomic force microscope (AFM) examinations.

2.7. Quantum chemical calculations

Quantum chemical calculations were carried out by density function theory (DFT) method B3LYP with all electron basis set 6-31G* on all atoms [13]. This theoretical level is denoted as