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Experimental and theoretical evaluation of two pyridinecarboxaldehyde thiosemicarbazone compounds as corrosion inhibitors for mild steel in hydrochloric acid solution

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ABSTRACT

The inhibition effect of two Schiff's base derivatives on the corrosion of mild steel in 1.0 M HCl solution was studied by electrochemical techniques, SEM and theoretical calculation methods. The experimental results show that the inhibition efficiency of 2-pyridinecarboxaldehyde thiosemicarbazone (2-PCT) is higher than that of 4-pyridinecarboxaldehyde thiosemicarbazone (4-PCT), and both the two compounds are good inhibitors for mild steel in 1.0 M HCl. Potentiodynamic polarization curves show that the two inhibitors act as mixed type inhibitors. The adsorption of inhibitors obeys the Langmuir adsorption isotherm, and the thermodynamic parameters (E_a, K_{ads}, ΔG^0_{ads}) were calculated and discussed. The mechanism of inhibition was determined by PZC measurements and theoretical calculation methods.

1. Introduction

Mild steel, widely used in engineering applications, is highly susceptible to corrosion, especially in acidic media [1,2]. As acidic media, the use of hydrochloric acid solution in acid pickling, industrial cleaning, acid descaling and acidization of oil wells is more economical, efficient and trouble-free, compared to mineral acids [3,4]. Because of the strong corrosivity of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metal surface. In recent years, there is a considerable amount of effect devoted to finding the efficient corrosion inhibitors. It is well known that heterocyclic compounds, containing electronegative functional groups, π-electrons and heteroatoms like sulfur, nitrogen and oxygen as well as aromatic rings in their structures, often show good corrosion inhibitive ability in acid media [5–8]. The electron-rich structure serves as potential adsorption sites, due to their capability to share free electrons with the metal substrate surface [9]. Nowadays, the study of Schiff's base inhibitors is a hot topic [10,11]. Due to the planarity structure and lone pair of electrons present on the N atoms in the presence of >C=N— groups, the Schiff's base inhibitors show good corrosion inhibition efficiencies.

Quantum chemical calculations have been proved to be a very powerful tool for studying the correlation of the molecular structure of inhibitors and the inhibition properties [12,13]. Meanwhile, molecular dynamics (MD) method, often utilized to study the

interaction of phase interfaces [12,14], has been applied to research the interaction between inhibitors and metal surface. The MD simulations can provide insights into the design of inhibitor systems with superior properties and elucidate the adsorption process at molecular level [15,16].

2-pyridinecarboxaldehyde thiosemicarbazone (2-PCT) and 4-pyridinecarboxaldehyde thiosemicarbazone (4-PCT) are Schiff's base compounds with heterocyclic structures consisting of N, S atoms and conjugated double bonds. The aim of this study is to report on the inhibition effects of 2-PCT and 4-PCT on the corrosion behavior of mild steel in 1.0 M HCl media utilizing electrochemical techniques, scanning electron microscopy (SEM) and theoretical calculation methods. Besides, an attempt is made to elucidate the inhibition mechanism by studying the potential of zero charge (PZC).

2. Experimental

2.1. Materials and sample preparation

Two Schiff's base derivatives, namely 2-pyridinecarboxaldehyde thiosemicarbazone (2-PCT) and 4-pyridinecarboxaldehyde thiosemicarbazone (4-PCT) shown in Fig. 1, were synthesized in laboratory according to the following procedures [5,17]. 2-Pyridinecarboxaldehyde (0.01 mol) or 4-pyridinecarboxaldehyde (0.01 mol) was slowly dropwise to a mixture of thiosemicarbazide (0.01 mol), 40 mL ethanol and a catalytic amount of concentrated sulfuric acid (three drops), respectively, then the mixture solution

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2-pyridinecarboxaldehyde thiosemicarbazone (2-PCT)

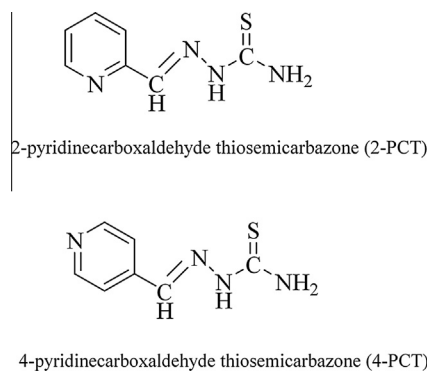4-pyridinecarboxaldehyde thiosemicarbazone (4-PCT)

Fig. 1. Chemical structures of the synthesized inhibitors.

was heated to 353.15 K. The reaction solution was stirred under reflux for 4 h and then cooled to room temperature. The obtained precipitate was collected and recrystallized by ethanol. The structures of the two compounds were characterized by ^{1}H NMR and FT-IR spectroscopic methods. For 2-PCT: ^{1}H NMR (DMSO-d$_6$, 500 MHz), δ: 7.35–7.38 (m, 1H, PyH), 7.80–7.83 (m, 1H, PyH), 8.09 (s, 1H, N=CH), 8.14 (s, 1H, NH$_2$), 8.26 (d, 1H, PyH), 8.32 (s, 1H, NH$_2$), 8.56 (d, 1H, PyH), 11.61 (s, 1H, NNHC=S); IR (KBr) υ: 3434, 3260, 3157, 1608, 1526, 1111, 878, 620, 419 cm^{-1}. For 4-PCT: ^{1}H NMR (DMSO-d$_6$, 500 MHz), δ: 7.78 (d, 2H, PyH), 8.04 (s, 1H, N=CH), 8.21 (s, 1H, NH$_2$), 8.40 (s, 1H, NH$_2$), 8.60 (d, 2H, PyH), 11.69 (s, 1H, NNHC=S); IR (KBr) υ: 3419, 3261, 3152, 1596, 1539, 1107, 877, 633, 422 cm^{-1}. The appearance of peaks at 1608 cm^{-1} (2-PCT) and 1596 cm^{-1} (4-PCT), correspond to the >C=N— group, confirmed the formation of the Schiff's base.

The tests were performed in 1.0 M HCl solution and containing various concentrations of 2-PCT or 4-PCT. An aggressive solution (1.0 M HCl) was prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of the Schiff's base inhibitors employed was 0.15–1.5 mM, and the solution without inhibitors was prepared for comparison. Corrosion tests were performed on mild steel samples containing 0.17 wt.% C, 0.37 wt.% Mn, 0.20 wt.% Si, 0.03 wt.% S, 0.01 wt.% P and bal. Fe.

2.2. Electrochemical experiments

A conventional three-electrode cell system was utilized in all electrochemical measurements, with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. All potential values in this paper were referred to the SCE. In order to minimize the ohmic contribution, the Luggin capillary was kept close to the working electrode in the electrochemical measurements. The mild steel cylinder, embedded in epoxy resin with an exposed area of 0.5 cm^2 to the electrolyte, served as the working electrode (WE). Prior to all measurements, the WE surface was abraded with different emery papers (grade 320, 600 and 1200), washed with double distilled water, rinsed with acetone, and then dried with a cold air stream. The electrochemical measurements were performed with ZAHNER IM6ex electrochemical workstation, controlled by ZAHNER THALES software. The electrochemical impedance spectroscopy (EIS) measurements were carried out over the frequency range 100 kHz to 300 mHz at the open circuit potential by superimposing alternating current (AC) signal of 5 mV after immersion for 1 h in the corrosive media. The potentiodynamic polarization curves were recorded from −800 to −200 mV (vs. SCE) with a scan rate of 1.0 mV s^{-1}. All electrochemical tests have been carried out in non-deaerated solutions under unstirred conditions, and the temperature was controlled by using a thermostatic water bath. In order

to achieve good reproducibility, each electrochemical measurement was performed in triplicate, and the mean value of the experiments was reported in this manuscript.

2.3. Measurement of the potential of zero charge

The electrochemical impedance spectra were recorded at the AC amplitude of 5 mV and by applying different potentials. The values of double layer capacitance were plotted against the potentials to determine the PZC after immersing mild steel in 1.0 M HCl solutions containing 1.5 mM 2-PCT or 4-PCT for 1 h.

2.4. Scanning electron microscopy (SEM) studies

In order to get insight into the changes on surface of corrosive samples before and after the addition of inhibitors, the specimens were first immersed in 1.0 M HCl in the absence and presence of 1.5 mM 2-PCT or 4-PCT for 8 h at 30 °C, respectively, then taken out from the test solutions, cleaned with bi-distilled water and acetone, and dried with cool air. The SEM images were conducted using a Quanta200 scanning electronic microscope at high vacuum and 20.0 kV EHT.

2.5. Calculation methods

The molecular dynamics (MD) simulations were performed using the software, Material Studio 5.5, Discover module. Fe (110) surface was chosen for the simulation study. The MD simulation of the interaction between molecular PCT and the Fe (110) surface was carried out in a simulation box (19.86 Å × 19.86 Å × 38.10 Å) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary boundary effects. The Fe (110) plane was first cleaved from Fe crystal, and then the surface was optimized to the energy minimum. The addition of the Schiff's base molecules near to the surface was carried out and using the PCFF force field to simulate the behavior of the PCT molecules on the Fe (110) surface. The MD simulation was performed under 298 K, NVT ensemble, with a time step of 0.1 fs and simulation time of 50 ps. The interaction energy $E_{interaction}$ of the Fe surface with the PCT molecules was calculated according to the following equation:

$$E_{interaction} = E_{total} - (E_{surface} + E_{PCT}) \tag{1}$$

where E_{total} is the total energy of Fe crystal together with the adsorbed PCT molecules, $E_{surface}$ and E_{PCT} are the energy of the Fe crystal and free PCT molecules, respectively. And the binding energy is the negative value of the interaction energy, $E_{binding} = -E_{interaction}$.

Quantum chemical calculations were conducted with DMol^3 module in Materials Studio software. All electron calculations of PCT molecules were accomplished by GGA/BLYP method with a double zeta plus polarization (DNP) basis set and the choice of convergence accuracy was fine. Frequency analysis was performed to ensure the calculated structure being the minimum point on potential energy surface (without imaginary frequency).

3. Results and discussion

3.1. Potentiodynamic polarization measurements

The potentiodynamic polarization curves of mild steel in 1.0 M HCl with and without various concentrations of 2-PCT and 4-PCT are shown in Fig. 2. It can be seen from the figures that the presence of inhibitors causes a prominent decrease in the corrosion rate, i.e. shifts both anodic and cathodic Tafel curves to lower values of current densities. This phenomenon indicates that both anodic metal dissolution and cathodic hydrogen evolution reaction are