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Corrosion inhibition of a new Schiff base derivative with two pyridine rings on Q235 mild steel in 1.0 M HCl

Yan Ji[a], Bin Xu[a,b], Weinan Gong[a], Xueqiong Zhang[a], Xiaodong Jin[a], Wenbo Ning[a], Yue Meng[a], Wenzhong Yang[a,*], Yizhong Chen[c]

[a] College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 210009, China
[b] Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, Nanjing 210042, China
[c] School of Environmental and Safety Engineering, Jiangsu Polytechnic University, Changzhou 213164, China

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ABSTRACT

A new Schiff base derivative, namely 4-(((4-(bis(pyridin-2-ylmethyl) amino) phenyl) imino) methyl)-N,N-diethylaniline, with more than one pyridine ring and two benzene rings was synthesized successfully. And then its corrosion inhibition properties were estimated in 1.0 M HCl by weight loss experiments, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The results showed that 4-(((4-(bis(pyridin-2-ylmethyl) amino) phenyl) imino) methyl)-N,N-diethylaniline is a mixed type inhibitor and follows Langmuir adsorption isotherm. SEM-EDX and XPS techniques were used for surface analysis. Meanwhile, quantum chemical calculation using density functional theory (DFT) established the correlation between the structure and corrosion inhibition efficiency. Molecular dynamic simulation was adopted to investigate the adsorption behavior on mild steel surface.

1. Introduction

Hydrochloric acid solution is widely used in various industries for a lot of purposes, such as acid cleaning, acid pickling and acid descaling [1–3], which may lead to corrosion phenomenon. In recent years, corrosion of metals has attracted many investigations. In order to reduce the loss of corrosion, corrosion inhibitors are generally employed, which is one of the most effective and economic method for controlling metal dissolution [4]. It is generally accepted that in acid media inhibitors adsorb on the metal surface by displacing H_2O molecules and form a protection film. Schiff base, containing –C=N– structure, has been proved to be effective corrosion inhibitors for metals in acidic media [5–7]. In its structure, N atom is capable to form coordinate-covalent bonds with metals due to its lone pairs of electrons. While the π-bond can interact with the metal surface, which results in good adsorption ability of Schiff base derivatives. A survey of literature reveals that the pyridine is an effective corrosion inhibitor and its derivatives have received a considerable amount attention on their inhibition properties, like 2-amino-3, 5-dicarbonitrile-4-(4-nitrophenyl)-6-(phenylthio) pyridine [9], 2-(4-pyridyl)-benzimidazole [10], pyridine-2-thiol [11], 6-methyl-4,5-dihydro-2H-pyridazine-3-one, 6-phenyl-2H-pyridazine-3-one and 6-phenyl-2H-pyridazine-3-thione [12]. The existing results showed that pyridine derivatives can inhibit the metal dissolution through N atom and electron rich structure, which can enhance adsorption ability. However, most studied substances contained only one pyridine ring, and the researches on the pyridine derivatives with two or more pyridine rings are rare [13]. Meanwhile, the increasing number of the aromatic rings may affect space steric and the aromaticity of a corrosion inhibitor. So it is difficult to predict the corrosion inhibition ability of a substance with Schiff base structure and more than one pyridine ring. The studied inhibitor, 4-(((4-(bis(pyridin-2-ylmethyl)amino)phenyl)imino)methyl)-N,N-diethylaniline (BPMA), contains a Schiff base character structure and two pyridine rings, which is worth investigating.

In the past two decades, quantum chemical calculations have been widely used to testify the relationship between quantitative molecular structures and molecular chemical properties. The density functional theory (DFT) is the most popular calculation method in computational chemistry [1,14,15,16]. In addition, the molecular dynamics simulations can provide the information of both the configuration and absorption energy which has been emerged as a convenient and effective tool to study the adsorption behavior of corrosion inhibitor molecules on metal surface in specific conditions [17,18].

In this paper, we synthesized BPMA and ensured its molecular structure by ^{1}H NMR, ^{13}C NMR, and MS. Then weight loss measurements and electrochemical experiments were employed to

* Corresponding author. Fax: +86 25 83172359.
E-mail address: yangwznjtech@163.com (W. Yang).

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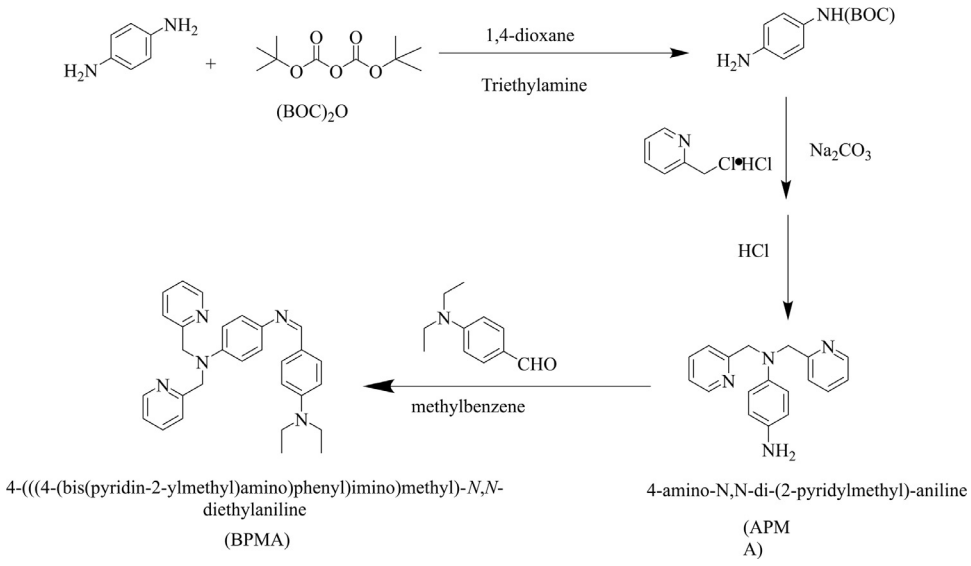

Scheme 1. Synthetic route and structure of BPMA.

analysis the inhibition effect of BPMA on the metal surface in 1.0 M HCl solution. Quantum chemical calculations and molecular dynamic simulations were carried out to estimate the interaction between the studied inhibitor and mild steel surface.

2. Experimental

2.1. Synthesis of inhibitor

The studied inhibitor, BPMA, was synthesized according to the synthetic route shown in Scheme 1.

The preparation of the intermediate product 4-amino-N, N di-(2-pyridylmethyl)-aniline (APMA) has been previously described [13], and the identification of the structure was performed. 4-Diethylaminobenzaldehyde (DEAM) was added to the solution of the APMA in dry methylbenzene, and the mixture was heated reflux at 120 °C for 24 h. The resulting solution was purify by toluene recrystallization. ^{1}H NMR, ^{13}C NMR, and MS were used as characterization methods to determine the structure. The results (see ESI, Figs. S1–S3 †) confirmed that the substance was our target. ^{1}H NMR (300 MHz, DMSO-*d*6): δ 1.10 (m, 6H), 3.37(m, 4H), 4.83(s, 4H), 6.67(m, 4H, Ar–H), 7.01(d, 2H, pyridine–H), 7.28(m, 4H), 7.59(m, H, Ar–H), 7.73(m, 2H), 8.30(s, 1H), 8.55(d, 2H, –C–N). 13C NMR (500 MHz, DMSO-*d*6): δ 158.99, 155.65, 149.24, 145.85, 141.39, 136.67, 123.66, 122.04, 121.05, 114.06, 112.67, 110.81, 57.12 43.69, 38.94, 12.36. MS (ESI) *m*/*z* (%) 450.2 (100) $M^{+}+H$.

2.2. Weight loss measurements

The corrosion tests were performed using 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 balance iron. The steel coupons were mechanically cut into 5.00 cm × 2.50 cm × 0.20 cm dimensions for weight loss experiments, and the weight loss experiments were conducted in glass cells of 500 mL solution volume. Prior to experiments, the coupons were cleaned with ethanol and ultrapure water, and finally dried in room temperature and weighed. Then the coupons were immersed in 1.0 M HCl for 16 h with different concentrations of the synthesized substance without stirring at different temperatures (303, 308, 313 and 323 K). The temperature of the solution was controlled by a water thermostat. After the corrosion experiments, the coupons were taken out, carefully washed with ultrapure water and ethanol, dried in room temperature and then weighed.

2.3. Electrochemical measurements

A classical three-electrode cell was employed in all electrochemical measurements, with a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode and a platinum sheet electrode as the auxiliary electrode. The mild steel coupon, embedded in Teflon holder using epoxy resin with an exposed area of 0.79 cm^2, served as the working electrode (WE). Prior to each electrochemical experiment, the WE was abraded using various grades of emery papers (200,500, 1200, 1500 and 2000 grit), cleaned with double distilled water, and followed by a rinse in acetone.

The electrochemical experiments were carried out with a ZAHNER IM6ex electrochemical workstation, controlled by ZAHNER THALES software. The electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit potential over the frequency range of 100 kHz–100 mHz by superimposing a sinusoidal alternating current signal of 5 mV after immersion in the corrosive media for 0.5 h. The potentiodynamic polarization curves were obtained by a sweep rate 1.0 mV/s, recorded from −700 to −300 mV (*vs.* SCE). All the tests were conducted in naturally aerated solution under unstirred conditions, and the temperature was controlled by a thermostatic water bath. In order to achieve good reproducibility, all electrochemical measurements were performed in triplicate, and only the mean value was reported in this manuscript.

2.4. Surface analysis

To get insight into the change of metal surface after immersion in 1.0 M HCl with and without BPMA for 12 h at 30 °C. The SEM examination was conducted using a JSM-6510 scanning electron microscope and the EDX was employed to analysis the chemical composition of the specimens on NORAN VANTAGE DSI instrument.

X-ray photoelectron spectroscopy (PHI 5000) was recorded for the adsorption of BPMA on the mild steel surface, employing Al Kα X-ray source (1486.4 eV) and the binding energy of Ag 3d5/2 (368.2 eV) was used as a reference.

2.5. Density functional theory details

In the present study, the popular Becke's three-parameter hybrid functional (B3LYP) method [19–22] and 6-31G (d) basis set [23,24] were used to optimize the geometry structure of the