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Experimental and theoretical evaluation of N, N-Bis(2-pyridylmethyl)aniline as a novel corrosion inhibitor for mild steel in hydrochloric acid

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ABSTRACT

The inhibition performance of a pyridine derivative with more than one pyridine ring, N, N-Bis(2-pyridylmethyl)aniline (BPA), for mild steel in 1.0 M HCl was evaluated by weight loss, electrochemical measurements and scanning electron microscopy methods. Then the experimental results were confirmed by quantum chemical calculations and molecular dynamics simulations methods. It was found that BPA behaved as a mixed type inhibitor, retarding both anodic metal dissolution and cathodic hydrogen evolution reactions. The adsorption process of BPA obeyed the Langmuir isotherm and the thermodynamic parameters were discussed. The scanning electron microscopy study proved that BPA can exhibit good inhibition ability by forming a protective film on the mild steel surface.

1. Introduction

Up to now, various nitrogen-containing heterocyclic organic compounds have been found to be effective corrosion inhibitors for mild steel in acidic media, *e.g.* pyrrole [1], pyrimidine derivatives [2], pyrazole derivatives [3,4], indole derivatives [5,6]. It is generally accepted that the adsorption characteristics of heterocyclic organic compounds are affected by the structures of the organic molecules, such as functional groups, steric factor and aromaticity [7]. Furthermore, the inhibition efficiency of nitrogen-containing heterocyclic organic inhibitors always increases with the number of aromatic systems and the availability of electronegative atoms in the molecules [7–9]. Pyridine is a basic heterocyclic organic compound, which is structurally related to benzene, with one methine group replaced by a nitrogen atom. The nitrogen atom and electron-rich structure facilitate the adsorption behavior onto the metal surface. Recently, the corrosion inhibition study of pyridine derivatives has been a hot topic, like 2-amino-3,5-dicarbonitrile-6-thio-pyridine [10], 2-amino-5-(*n*-pyridyl)-1,3,4- thiadiazole [11], 2-pyridyl disulfide, pyridine-2-thiol [12], 2-pyridinecarbonitrile [13], 2-amino-4-methylpyridine [14], 2-(4-pyridyl)-benzimidazole [15], N'-(phenylmethylene) isonicotinohydrazide, N'-(2-hydroxybenzylidene) isonicotinohydrazide [16] and so on. However, the most studied pyridine derivatives contain simple molecular structures and only one pyridine ring. The compounds with two or more pyridine segments are rarely investigated. Therefore, it is necessary to study the corrosion inhibition effect and inhibition mechanism of the pyridine derivatives with more than one pyridine ring which could be deemed as good potential inhibitors. The studied inhibitor, N, N-Bis(2-pyridylmethyl)aniline (BPA), is a pyridine derivative compound with two pyridine rings and a benzene ring, which should be a good inhibitor and show better inhibition effect than pyridine. Meanwhile, the use of quantum chemical calculations supported by the molecular dynamics simulations method has been proved to be an effective modern tool in elucidating the mechanism of inhibition of corrosion inhibitors on metal surface at the molecular level [17,18].

In this paper, we employed electrochemical techniques, weight loss and scanning electron microscopy methods to study the inhibition effect of BPA for mild steel in 1.0 M HCl solution. And then, quantum chemical calculations and molecular dynamics simulations method were performed to elucidate the interaction between the inhibitor molecules and mild steel surface.

2. Experimental

2.1. Materials

The studied inhibitor, BPA (Fig. 1), was synthesized according to a previously reported literature [19]. A solution of 4-aminophenyl

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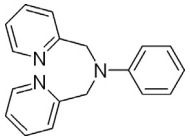

Fig. 1. Chemical structure of BPA.

(10 mmol) in N, N-diisopropylethylamine stirred well under N_2 atmosphere. 2-(Chloromethyl)-pyridine hydrochloride (40 mmol) was then added, and the mixture was heated to reflux at 80 °C for 24 h. The resulting brown suspension was filtered, and the solvent was removed in vacuo to yield brown oil. The brown oil was diluted with CH_2Cl_2, and then the organic layer was washed with brine, dried over Na_2SO_4, and the CH_2Cl_2 was removed under vacuum. The crude product was run through a silica plug to give the desired product as an orange solid. The structure of the compound was characterized by ^1H NMR and FT-IR spectroscopic methods (Fig. 2). ^1H NMR (300 MHz, $CDCl_3$), δ: 4.83 (s, 4H, $-CH_2-N-$), 6.69 (m, 3H, Ar–H), 7.15 (m, 4H, het–H), 7.26 (d, 2H, Ar–H), 7.60 (t, 2H, het–H), 8.58 (d, 2H, het–H). IR (KBr) υ: 3451, 3090, 3052, 2923, 1586, 1503, 1466, 1430, 1381, 1352, 1223, 1176, 1098, 1036, 992, 954, 803, 757, 694, 659 cm^{-1}.

Tests were performed with mild steel samples of the following chemical composition (wt. %): 0.17% C, 0.37% Mn, 0.20% Si, 0.03% S, 0.01% P and balance Fe. The test aggressive solution (1.0 M HCl) was prepared by dilution of analytical grade 37% HCl with double distilled water. The employed concentration range of BPA was 0.5–3.0 mM, and the blank solution without BPA was prepared for comparison.

2.2. Weight loss experiments

The weight loss experiments were conducted in glass cells of 500 mL solution volume. The mild steel coupons were mechanically cut into 5.00 cm × 2.50 cm × 0.20 cm dimensions for weight loss experiments. 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 18 h with different concentrations of BPA without stirring at (303 ± 1) K. The solution temperature was controlled by a water thermostat. After the corrosion experiments, the coupons were taken out, carefully washed with ultrapure water and ethanol, dried and then weighed.

2.3. Electrochemical measurements

A conventional three-electrode cell system was employed in all electrochemical experiments. A mild steel disk, embedded in epoxy resin, with an exposed area of 0.785 cm^2 to the electrolyte was used as the working electrode (WE) and a Pt electrode was used as an auxiliary electrode, respectively. A saturated calomel electrode (SCE) coupled to a fine Luggin capillary was served as the reference electrode. In order to drop down the ohmic contribution, we kept the

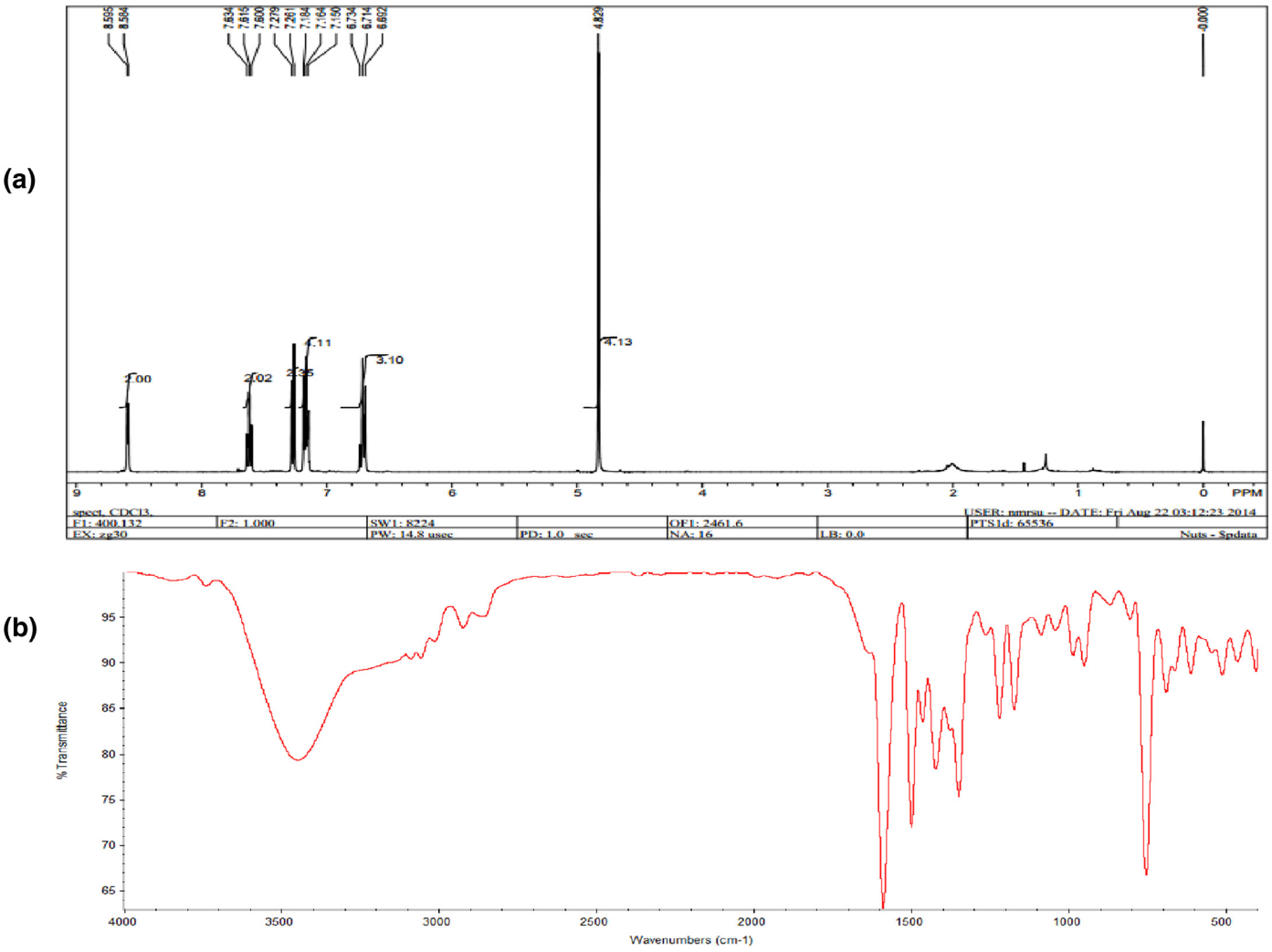

Fig. 2. ^1H NMR (a) and FTIR (b) spectra of BPA.

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