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1,2,3-Triazole derivatives as corrosion inhibitors for mild steel in acidic medium: Experimental and computational chemistry studies

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ABSTRACT

(1-Benzyl-1H-1,2,3-triazole-4-yl)methanol (BTM) and (1-(pyridin-4-ylmethyl)-1H-1,2,3- triazole-4-yl)methanol (PTM) were prepared and investigated as corrosion inhibitors for mild steel in 1.0 M HCl. It is found that PTM functions as more effective inhibitor than BTM in the concentration range of 0.2 −1.0 mM. Computational chemistry studies show that the triazole derivatives can adsorb on the mild steel surface by sharing the lone pair electrons of N atoms with iron atoms or by accepting electrons from iron surfaces. Due to its strong interaction with the mild steel surface in aqueous system, the pyridine segment should be responsible for the higher inhibition efficiency of PTM.

1. Introduction

Corrosion inhibition efficacy of organic inhibitors strongly depends on their adsorption properties [1,2]. It has been reported that adsorption is mainly related to the presence of π-electrons of aromatic rings and heteroatoms in the molecular structures [3–6]. Based on that, the organic compounds containing nitrogen, sulfur and oxygen atoms have attracted more and more attention in the studies on corrosion inhibition of mild steel in acidic media [7–11]. A typical example is triazole derivatives, especially 1,2,4-triazole derivative. Actually, unmodified 1,2,4-triazole is not a good corrosion inhibitor for mild steel in acidic solution [12]. A common pathway to enhance the inhibition efficiency is to modify the structures of the triazole compounds with various substituents. Lagrenée et al. synthesized a serial of 3,5-disubstituted 1,2,4-triazole compounds and found the triazole derivatives exhibit excellent corrosion inhibition efficacy [13–20]. It has been observed that, moreover, 3 and/or 4-substituted triazole derivatives by thiol- or amino-group can function as highly efficient corrosion inhibitors because the modifications of those groups make stronger adsorptive layers of the triazole compounds on mild steel [21–30]. In addition, Schiff's base derivatives of triazole have also been investigated as corrosion inhibitors of mild steel in acidic medium [31–34].

Regardless of the wide investigation on 1,2,4-triazole compounds as corrosion inhibitors of mild steel in acidic solutions, much less attention has been paid to 1,2,3-triazole derivatives. Recently, several studies have shown that 1,2,3-triazole derivatives with various substituents can strongly adsorb on mild steel surface and achieve adequate corrosion inhibition efficiency at a low concentration [35–37]. However, there is still a lack of interaction mechanism between 1,2,3-triazole derivatives and metal surface.

In the present study, we synthesize two new 1,2,3-triazole derivatives, (1-benzyl-1*H*-1,2,3-triazole-4-yl)methanol (BTM) and (1-(pyridin-4-ylmethyl)-1*H*-1,2,3- triazole-4-yl)methanol (PTM) as shown in Fig. 1, and investigate their corrosion inhibition for mild steel in 1 M HCl solution. Based on the theoretical study, furthermore, we attempt to clarify the interaction between the triazole derivatives and iron surface and to understand the difference in inhibition efficiency between BTM and PTM.

2. Experimental and computational details

2.1. Synthesis of BTM and PTM

BTM and PTM were prepared through a modified procedure reported previously [38,39], as shown in Fig. 1.

2.1.1. Benzyl azide

To a solution of benzyl chloride (2.291 mL, 0.02 mol) and water (4 mL) in DMSO (20 mL), sodium azide (2.600 g, 0.04 mol) was added. The resulting mixture was stirred at room temperature for 24 h, and then the reaction mixture was extracted with petroleum ether (30 mL × 4). The combined organic layer was washed with water (30 mL × 2) and saturated brine (30 mL), respectively, and then was dried over anhydrous Na_2SO_4. After removing the desiccant by

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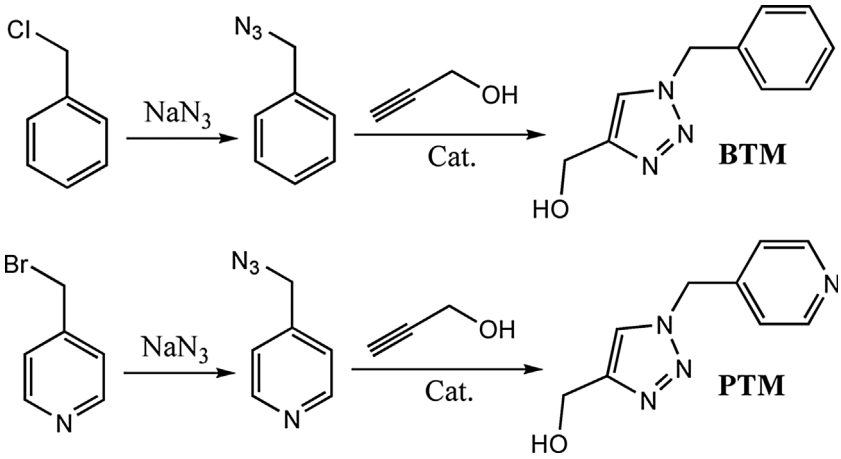

Fig. 1. Synthesis routes of BTM and PTM.

filtration, the mixture was evaporated in vacuo to give colorless oily liquid. The product was used without further purification in the next reaction. Yield 2.370 g (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.30 (m, 5H, Ar*H*), 4.32 (s, 2H, CH_2)

2.1.2. (1-benzyl-1H-1,2,3-triazole-4-yl)methanol (BTM)

Propargyl alcohol (0.640 mL, 11 mmol) was added to a mixture of benzyl azide (1.330 g, 10 mmol), $CuSO_4$ (0.500 g, 2 mmol) and sodium ascorbate (0.790 g, 4 mmol) in ^{t}BuOH:H_2O (10 mL:10 mL). The resulting yellow mixture was stirred at room temperature for 16 h under an atmosphere of nitrogen. Then the reaction mixture was diluted and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with water (30 mL × 2) and saturated brine (20 mL), respectively. The organic phase was then dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to give acicular solid. Yield: 1.342 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H, N−C*H*), 7.38-7.34 (m, 3H, CH_{Ar}), 7.27-7.24 (m, 2H, CH_{Ar}), 5.49 (s, 2H, Ar-CH_2), 4.73 (s, 2H, CH_2), 3.58 (bs, 1H, O*H*).

2.1.3. 4-(azidomethyl)pyridine

To a solution of 4-(bromomethyl)pyridine hydrobromide (1.000 g, 3.95 mmol) and potassium carbonate (0.550 g, 3.95 mmol) in DMF (10 mL). Then sodium azide (0.390 g, 5.93 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. Afterwards the resulting reaction mixture was diluted and extracted with CH_2Cl_2 (40 mL × 3). The combined organic layers were washed with water (30 mL x 2), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to give oily liquid. Yield: 0.470 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63-8.62 (m, 2H, C*H*-N−C*H*), 7.27-7.24 (m, 2H, C*H*-C−C*H*), 4.40 (s, 2H, N_3−CH_2).

2.1.4. (1-(pyridin-4-ylmethyl)-1H-1,2,3-triazole-4-yl)methanol (PTM)

Propargyl alcohol (0.256 mL, 4.4 mmol) was added to a mixture of 4-(azidomethyl)pyridine (0.536 g, 4 mmol), $CuSO_4$ (0.128 g, 0.8 mmol) and sodium ascorbate (0.316 g, 1.6 mmol) in ^{t}BuOH:H_2O (10 mL:10 mL). The resulting yellow mixture was stirred at 50 °C for 16 h under nitrogen, and then was diluted and extracted with ethyl acetate (30 mL × 3). The organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to give white solid. Yield: 0.228 g (30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, 2H, C*H*-N−C*H*), 7.57 (s, 1H, N−C*H*-C), 7.10 (d, 2H, C*H*-C−C*H*), 4.80 (s, 2H, N_3−CH_2), 3.97 (bs, 1H, O*H*).

2.2. Corrosion inhibition tests

2.2.1. Weight loss measurements and surface morphology

Mild steel specimens containing 0.17 *wt.*% C, 0.20 *wt.*% Si, 0.37 *wt.*% Mn, 0.03 *wt.*% S, 0.01 *wt.*% P, and balance iron were cut into coupons with the size of 5.0 cm × 2.5 cm × 0.2 cm. Weight loss tests were carried out in non-deaerated solutions. The coupons were fully immersed in 1.0 M HCl solutions containing various concentrations of the inhibitors at 25 ± 0.1 °C for 8 h. After being withdrawn from the test solutions, the mild steel specimens were washed with deionized water, scrubbed with absorbent cotton to remove the corrosion products on the surfaces and then washed with anhydrous ethanol, followed by drying at room temperature. Finally, the specimens were weighed for the calculation of corrosion rate.

After weight loss tests, the surfaces of the specimens were immediately examined by both atomic force microscope (AFM, Nanosurf FlexAFM, Switzerland) and scanning electron microscope (SEM, Hitachi S-4800, Japan). For AFM measurements, the surface morphology on a 50 μm × 50 μm scale was scanned in tapping mode using silicon cantilevers with a resonance frequency of 120–250 kHz and a force constant of 20–100 N/m. All images were processed using a C3000 software of Nanosurf. For SEM measurements, an accelerating voltage of 5000 V was applied.

2.2.2. Electrochemical tests

Electrochemical impedance spectroscopy (EIS) measurements were carried out using the classical three-electrode system where the counter electrode was a platinum electrode and a saturated calomel electrode (SCE) was used as reference. To reduce Ohmic polarization, a Luggin capillary was connected to the reference. An epoxy-encapsulated mild steel electrode with the exposed area of 0.785 cm^2 was employed as working electrode. Prior to use, the mild steel electrode was abraded with SiC sandpapers (up to 2000 grit), rinsed with deionized water and ethanol successively and finally dried under nitrogen. Before EIS measurements, the mild steel electrode was immersed in the test solutions under unstirred condition for 60 min until a steady potential. EIS measurements were performed at open-circuit potential (OCP) over the range of 0.01 Hz to 100 kHz with the amplitude of 5 mV for the sine wave signal. All EIS data were analyzed by Zview software.

2.3. Quantum chemical method

Density functional theory (DFT) calculations were performed to optimize the geometries of inhibitor molecules using Dmol^3 module in Materials Studio software 6.0. In the DFT calculations, the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) formula was used for the electronic exchange-correlation potential [40], and all electron calculations were performed with double-numeric basis set (DNP 4.4) [41]. Geometry optimizations were performed without any symmetry constraint and vibrational analysis was carried out to ensure the optimized structures being the minimum point on potential energy surface.