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Theoretical prediction and experimental study of 1-Butyl-2-(4-methylphenyl)benzimidazole as a novel corrosion inhibitor for mild steel in hydrochloric acid

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ABSTRACT

The inhibition performance of a newly synthesized benzimidazole derivative, 1-Butyl-2-(4-methylphenyl)benzimidazole (BMPB), on the surface of mild steel in 1.0 M HCl was predicted theoretically using molecular dynamics method and quantum chemical calculations in comparison with benzimidazole (BI) compound. The theoretical results confirmed by electrochemical measurements and scanning electron microscopy study show that BMPB may exhibit better inhibitive performance than BI for mild steel in hydrochloric acid solution. The adsorption process and thermodynamic parameters of BMPB were calculated and discussed. It was found that BMPB is classified as a mixed type inhibitor, suppressing both anodic metal dissolution and cathodic hydrogen evolution reactions. The high inhibitory efficiency of BMPB is due to the formation of a protective film on the mild steel surface. This study shows that theoretical calculations can be used as a reliable method to select organic inhibitors prior to experiments.

1. Introduction

Hydrochloric acid solution is one of the most widely used agents for industrial acid cleaning, oil well acidizing, acid descaling and so on [1–3]. The metal dissolution in the corrosive media leads to economic losses, decreasing the lifetime of equipment and wasting resources. Inhibitors are generally used to reduce the rate of metal dissolution. The existing data show that organic inhibitors, containing heteroatoms, unsaturated bonds, or plane conjugated system, may exhibit good inhibition ability by forming a protective film on metal surface [4–7]. Theoretical chemistry has been widely used to explain the inhibition mechanism, including quantitatively characterizing the electronic structures of organic inhibitors and a rigorous modeling of the interaction between metal surface and inhibitors [8–10]. Quantum chemical calculation is a useful tool for investigating the molecular structure as well as elucidating the electronic properties [11,12]. Meanwhile, the molecular dynamics (MD) simulations can provide insights into the design of inhibitor systems with superior properties and elucidate the adsorption process at molecular level [13–15]. However, the use of theoretical methods in predicting inhibition efficiency of organic compounds as inhibitors for metals and thereafter confirmed by experimental studies is scarce in the previous literature [16,17].

BI is a heterocyclic aromatic organic compound with a bicyclic structure consisting of the fusion of benzene and imidazole rings [18]. The molecular structures of this substance and its derivatives are likely to facilitate the adsorption action on the metal surface. A perusal of literature [4,18–21] revealed that many benzimidazole derivatives are effective inhibitors for metal in aggressive solution, and they may perform different inhibitive properties with the differences in substituent positions on the imidazole ring and the different substituent groups. Nevertheless, the studies on 1-alkyl-2-substituted benzimidazoles as corrosion inhibitors are scanty. In the present work, we employed MD method and quantum chemical calculations to predict the inhibition performance of a newly synthesized benzimidazole derivative, BMPB (Fig. 1), for mild steel in 1.0 M HCl solution in comparison with BI. And then, the inhibition performance of BMPB for mild steel in 1.0 M HCl was validated experimentally by utilizing electrochemical techniques and scanning electron microscopy method.

2. Experimental

2.1. Materials

The studied inhibitor, namely BMPB, was synthesized according to a previously reported procedure [22] and characterized by ^{1}H NMR,

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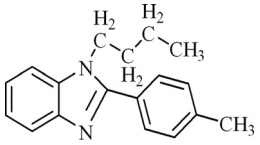

Fig. 1. Chemical structures of BMPB and BI.

^{13}C NMR and elemental analysis: Yield: 91.4%; m.p. 62–63 °C; ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 0.87 (t, 3H, CH_3), 1.31-1.25 (m, 2H, CH_2), 1.83-1.77 (m, 2H, CH_2), 2.44 (s, 3H, CH_3), 4.22 (t, 2H, CH_2), 7.30-7.27 (m, 4H, Ar-H), 7.41-7.39 (m, 1H, Ar-H), 7.61 (d, 2H, Ar-H), 7.83-7.81 (m, 1H, Ar-H); ^{13}C NMR ($CDCl_3$, 300 MHz), δ: 153.77, 139.8 0.53, 31.83, 21.41, 19.94, 13.52. Anal. Calcd. For $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60; Found C, 81.75; H, 7.61; N, 10.63.

The chemical composition (wt. %) of mild steel samples was as follows: C = 0.17%; Mn = 0.37%; Si = 0.20%; S = 0.03%; P = 0.01% and Fe for balance. The test aggressive solution, 1.0 M HCl, was prepared using double distilled water and analytical grade 37% HCl. The concentrations of BMPB ranged from 0.09 mM to 0.57 mM, and the blank solution without BMPB was prepared for comparison.

2.2. Calculation methods

Quantum chemical calculations within the density functional theory (DFT) were conducted with DMol^3 module in Materials Studio software 5.5. Geometrical optimizations and frequency calculations were performed by the generalized gradient approximation (GGA) functional of Becke exchange plus Lee–Yang–Parr correlation (BLYP) method [23] in conjunction with a double zeta plus polarization (DNP) basis set. Fine convergence accuracy and global orbital cutoffs were employed. Considering the solvent effects, all the geometries were re-optimized at the BLYP/DNP level by using COSMO and H_2O was defined as the solvent. Frequency analysis was performed to ensure the calculated structure was the minimum point on potential energy surface (without imaginary frequency).

The MD simulations were carried out using the software, Material Studio 5.5, Discover module. We chose Fe (1 1 0) plane for the simulation study. The MD simulations were performed in a three-dimensional simulation box (19.86 Å × 19.86 Å × 38.11 Å) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary boundary effects. The iron crystal was first cleaved along the (1 1 0) plane, and thereafter the surface was optimized to the energy minimum. Then the addition of the inhibitor and water molecules near the surface was performed. The COMPASS force field was used to optimize the structures of the components of the system (Fe + water + BMPB), while all the bulk atoms in the Fe (1 1 0) plane were kept "frozen". The MD simulations were carried out at 298 K, NVT ensemble, with a time step of 0.1 fs and simulation time of 50 ps. The interaction energy $E_{interaction}$ between the iron surface and the inhibitor molecules was calculated according to the following equation:

$$E_{interaction} = E_{total} - \left(E_{surface+water} + E_{inh+water}\right) + E_{water} \quad (1)$$

where E_{total} is the total energy of the simulation system, $E_{surface+water}$ and $E_{inh+water}$ are the total energies of the system containing only the iron surface together with water molecules and the inhibitor together with water molecules, respectively. E_{water} is the total energy of water molecules.

2.3. Electrochemical measurements

The electrochemical measurements were performed by utilizing a traditional three-electrode cell system. A platinum sheet electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary were served as the auxiliary electrode and reference electrode (RE), respectively. All potential data reported were measured with respect to SCE. A mild steel cylinder with an exposed area of 0.5 cm ^{2} to the electrolyte was used as the working electrode (WE) and the rest of the WE was embedded in epoxy resin. Before the electrochemical measurements, the surface of WE was abraded using various grades of emery papers, which ended up to 2000 grade. Subsequently, the WE was washed with double distilled water, rinsed with acetone, and dried at room temperature. All the electrochemical experiments were carried out by using a ZAHNER IM6ex electrochemical workstation, and analyzed by ZAHNER THALES software. Prior to the electrochemical experiments, the WE was immersed into the test solution for 0.5 h until a steady-state (open circuit) potential was obtained. Then the potentiodynamic polarization measurements were carried out subsequently. The potentiodynamic polarization curves were scanned from −700 to −300 mV (vs. SCE) with a sweep rate of 1.0 mV s^{-1}. All the electrochemical experiments were carried out under air atmosphere in unstirred condition, and the temperature was controlled by using a thermostatic water bath.

2.4. Scanning electron microscopy (SEM) studies

The morphologies of specimens after immersed in 1.0 M HCl with and without 0.57 mM BMPB for 8 h at 30 °C were analyzed by using scanning electron microscopy (TM 3000) at high vacuum.

3. Results and discussion

3.1. Quantum chemical calculations

Quantum chemical calculation has been widely utilized to provide a molecular-level understanding of the relationship between the inhibitor structure and its inhibition behavior. With this method, the chemical reactivity of the inhibitor can be predicted with the analysis of the quantum chemical indices. The optimized equilibrium geometries of BMPB and BI are shown in Fig. 2 and the values of bond angle, bond length and torsion angle in the molecule are listed in Table 1. BI contains the fusion of benzene and imidazole rings, while BMPB contains one benzimidazole segment, one benzyl group and one butyl chain. It can be seen from Table 1 that the bond lengths of C—N in the imidazole rings of the two inhibitors are longer than the general C=N double bond (1.280 Å) and shorter than the general C—N single bond (1.470 Å). Meanwhile, in BMPB molecule, the bond length of C13—C16 is 1.514 Å, which is longer than the general C=C double bond (1.33 Å) and shorter than the general C—C single bond (1.54 Å). The tendency of average in the bond length is indicative of a conjugation effect in the imidazole ring and the benzyl group, resulting in the rigid planar structure of the benzimidazole segment. Naturally, BI shows a planar geometric structure and may adsorb on the iron surface in a horizontal manner [10]. Meanwhile, due to the free rotation of C—C single bonds in the molecule, BMPB shows a non-planar geometric structure, and the torsion angles of N7—C17—C18—C19 and N7—C9—C10—C15 are 177.71° and 136.04°, respectively. So it may be difficult for BMPB to adsorb on the mild steel surface in a completely horizontal manner.

The metal-inhibitor interactions of the organic molecules are closely related to the frontier molecular orbitals, which is useful in predicting adsorption centers of the inhibitor molecules [24]. Fig. 3 depicts the frontier molecular orbital density distributions of BI and BMPB, and the quantum chemical parameters like E_{HOMO} (the highest occupied molecular orbital energy), E_{LUMO} (the lowest unoccupied molecular orbital energy), ΔE (energy band gap, $\Delta E = E_{LUMO} - E_{HOMO}$), and μ (dipole moment) of BI and BMPB are listed in Table 2. From Fig. 3, it can be found that the electron density distributions of both HOMO and LUMO are almost entirely localized on the whole BI molecule, indicating a parallel adsorption of BI onto the metal surface. For BMPB, the electron density distributions of HOMO and LUMO are