Corrosion Science 102 (2016) 517–522

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Short communication

The inhibition performance of long-chain alkyl-substituted benzimidazole derivatives for corrosion of mild steel in HCl

Dongqin Zhang [a], Yongming Tang [a,*], Sijun Qi [a], Dawei Dong [a], Hui Cang [b], Gang Lu [c]

[a] School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, PR China
[b] College of Chemical Engineering and Biological, Yancheng Institute of Technology, Yancheng 224051, PR China
[c] College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, PR China

ARTICLE INFO

Article history:
Received 28 August 2015
Received in revised form 2 October 2015
Accepted 5 October 2015
Available online 14 October 2015

Keywords:
A. Mild steel
B. Modelling studies
B. Weight loss
C. Acid inhibition
C. Interfaces

ABSTRACT

The corrosion inhibition of a new benzimidazole derivative, 6-(dodecyloxy)-1*H*-benzo[*d*]imidazole (DBI), for mild steel in 1 M HCl was investigated in this paper. Computational chemistry was performed to explore the adsorption of DBI on metal surface. Inhibition performance of DBI is attributed to both the direct interaction of benzimidazole segment with iron surface and the barrier effect of the non-polar long chain against aggressive solution. Compared to the protonated form, the molecular form of DBI could more tightly interact with iron surface. These results show that the long-chain alkyl-substituted benzimidazole derivative is of great potential application as corrosion inhibitor.

1. Introduction

A continuing effort has been made to develop a corrosion inhibitor that exhibits a greater inhibition effect at a low concentration in the corrosion medium as well as environment-friendly feature [1]. In recent years, benzimidazole and its derivatives with low toxicity have received considerable attention as they provide effective corrosion inhibition due to strong adsorption on metal surface [2–6]. Benzimidazole, a heterocyclic aromatic organic compound, consists of the fusion of benzene and imidazole. The nitrogen atom and the aromatic ring in molecular structure are likely the facilitator of the adsorption of benzimidazole on the metallic surface [7–11]. However, relatively high concentration of benzimidazole is essential to achieve effective inhibition for steel in acidic medium. At the concentration of 10 mM, typically, the inhibition efficiency of benzimidazole for mild steel in 1 M HCl is only around 50% [5,12]. In hope of improving the inhibition effectiveness of benzimidazole, researchers have made a lot of attempts to develop new benzimidazole derivatives. Among all the benzimidazole derivatives, 2-substituted benzimidazole derivatives have been paid most attention to. It has been demonstrated that substitution of some groups including mercapto, alkyl, amino and aromatic groups etc. for 2-*H* of benzimidazole significantly enhances corrosion inhibition, as compared to benzimidazole [12–23]. Computational chemistry showed that those substituent groups, which enhance the electron-donating or electron-withdrawing properties of the active N atom on the heterocyclic ring, would strengthen or weaken the interaction with the metal surface [24–30]. In addition, several derivatives with substitution for 1-*H* of benzimidazole exhibit effective corrosion inhibition for mild steel in acidic medium as well [3,31].

Regardless of the mentioned derivatives, there are few reports on corrosion inhibition of the benzimidazole derivative with substituted group on benzene ring [32,33]. In the present work, we attempt to prepare a new benzimidazole derivative, 6-(dodecyloxy)-1*H*-benzo[*d*]imidazole (DBI), shown in Fig. 1 and to evaluate its corrosion inhibition for mild steel in 1 M HCl. In the structure of derivative, a long-chain alkyl group is connected to benzene ring of benzimidazole via oxygen atom. Evidently, there are two distinct segments in the structure: an alkyl chain as a non-polar tail and a benzimidazole segment as a polar head. This compound is expected to act as adsorption-type inhibitor as well as straight-chain amines [34].

* Corresponding author. Fax: +86 25 83587443.
E-mail address: tangym@njtech.edu.cn (Y. Tang).

http://dx.doi.org/10.1016/j.corsci.2015.10.002
0010-938X/

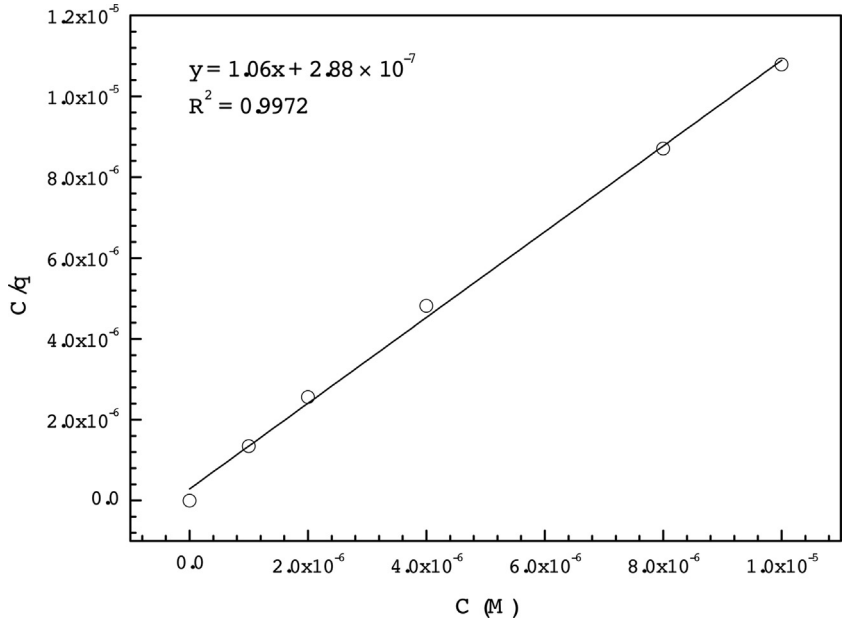

Fig. 2. Langmuir adsorption plot of the inhibitor in 1 M HCl at 25 °C.

2. Experimental and computational details

2.1. Corrosion measurements

Corrosion measurements were performed using mild steel coupons containing 0.17 wt.% C, 0.20 wt.% Si, 0.37 wt.% Mn, 0.03 wt.% S, 0.01 wt.% P and balance iron. Prior to use, the coupons with the size of $5.0 \times 2.5 \times 0.2\,cm^3$ were mechanically abraded up to 1000 grit, cleaned with ethanol and deionized water, and finally dried at room temperature. Weight loss measurements were carried out in a 250 mL vessel in a thermostat water bath held at the temperature of 25 ± 1 °C. The coupons were fully immersed in 1 M HCl solution containing various concentrations of the inhibitor. After 8 h of the immersion, the specimens were taken out, rinsed thoroughly with deionized water, scrubbed gently with a bristle brush to remove the corrosion product, washed successively with deionized water and ethanol, dried at room temperature and weighed. The inhibition efficiency (η) was calculated as follows:

$$\eta(\%) = \frac{v_0 - v}{v_0} \times 100 \quad (1)$$

where v_0 and v are the corrosion rate in the absence and presence of inhibitor, respectively. Duplicate experiments were performed in each case and both mean value and deviation of corrosion rate are reported.

2.2. Computational details

Density functional theory (DFT) calculations were performed to optimize geometries of the molecules without any symmetry constraint using D mol^3 module of Materials Studio software 6.0. All electron calculations of the molecules were performed using the generalized gradient approximation, following the Perdew-BuekeErnzerhof scheme (GGA/PBE), for the exchange-correlation functional. The "DNP" double-numeric basis set, which includes both d and p orbital polarization functions, was used in all calculations. And vibrational analysis was carried out to ensure the calculated structures reaching the minimum point on potential energy surface. In addition, the solvent (water) model was involved in all calculations.

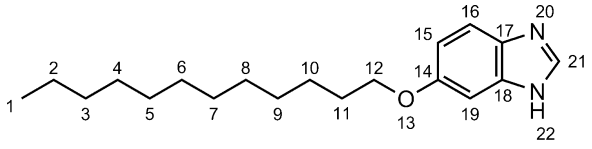

Fig. 1. Structure of DBI.

MD simulations were performed using Discover module of Materials Studio software 6.0. To construct the simulation box, the unit cell of iron was optimized to a minimum point of energy. A Fe (1 0 0) surface was cleaved from the bulk structure and optimized, and then the resulting cell was repeated ten times in the lateral directions (10×10). A water slab containing the studied compounds was then added near to the upper surface of the Fe slab. The size of the resulting box with periodic boundary conditions is $28.6 \times 28.6 \times 45.9\,Å^3$. MD simulations were performed using COMPASS force field as all Fe atoms were kept "frozen" at fixed positions and both inhibitor and water molecules were allowed to freely interact with the iron surface. A simulation temperature of 298 K and NVT ensemble with a time step of 0.1 fs and simulation time of 100 ps were implemented in all MD simulations. The interaction energy ($E_{interact}$) between Fe (1 0 0) and inhibitive molecule was calculated as follows:

$$E_{interact} = E_{tot} - (E_{surf+H_2O} + E_{inh}) \quad (2)$$

where E_{tot} is the total energy of simulation system, E_{surf+H_2O} is the energy of iron surface together with H_2O molecules, and E_{inh} is the energy of free inhibitive molecule.

3. Results and discussion

3.1. Corrosion inhibition of DBI

Table 1 depicts the corrosion rate of mild steel and inhibition efficiency from weight loss measurements in the absence and presence of DBI. It is clear that the corrosion rate of mild steel decreases significantly and the inhibition efficiency increases with increasing inhibitor concentration. Moreover, at a rather low concentration of the inhibitor, for instance, 8×10^{-6} M, the inhibition efficiency