Corrosion Science 87 (2014) 366–375

Contents lists available at ScienceDirect

Corrosion Science

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

Theoretical studies of three triazole derivatives as corrosion inhibitors for mild steel in acidic medium

Lei Guo [a], Shanhong Zhu [b], Shengtao Zhang [a,*], Qiao He [a], Weihua Li [c]

[a] *School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China*
[b] *School of Computer and Information Engineering, Xinxiang University, Xinxiang 453003, China*
[c] *Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China*

ARTICLE INFO

Article history:
Received 20 September 2013
Accepted 13 June 2014
Available online 22 June 2014

Keywords:
A. Mild steel
A. Acid solutions
B. Modelling studies
C. Acid inhibition

ABSTRACT

Corrosion inhibitive performance of 4-chloro-acetophenone-O-1′-(1′.3′.4′-triazolyl)-metheneoxime (CATM), 4-fluoro-acetophenone-O-1′-(1′.3′.4′-triazolyl)-metheneoxime (FATM), and 3,4-dichloro-acetophenone-O-1′-(1′.3′.4′-triazolyl)-metheneoxime (DATM) during the acidic corrosion of mild steel surface was investigated using density functional theory (DFT). Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), Mulliken charges, hardness (ξ), dipole moment (μ), and the fraction of electrons transferred (ΔN), were calculated. Quantitative structure activity relationship (QSAR) approach has been used, and a composite index of above-mentioned descriptors was performed to characterize the inhibition performance of the studied molecules. Furthermore, Monte Carlo simulation studies were applied to search for the best configurational space of iron/triazole derivative system.

1. Introduction

Metal destruction by corrosion leads to large maintenance costs in many industries. The protection of metals from corrosion is a challenging task for materials science in view of increasing environmental requirements. It has been known for some time that chromates, metasilicates, and molybdates are very good inhibitors of pitting corrosion in metals [1,2]. Besides, heterocyclic organic compounds consisting of a π-system and/or N, O, S heteroatoms have proven to be another source of effective inhibitors against corrosion, especially for steel in acidic medium [3–7]. Many authors have reported that the general trend in the inhibition efficiencies of molecules containing heteroatoms is such that $O < N < S < P$ [8–10]. This can be explained by the electronegativity of the atoms involved. Most of studies indicated that the inhibition of the corrosion processes is mainly due to formation of donor–acceptor complexes on the iron surface and the organic inhibitors σ-electron donation [11–14]. Among the various nitrogenous compounds studied as inhibitors, substituted triazole compounds are considered to be an excellent class of inhibitors to reduce corrosion rates and hydrogen embrittlement of steel and copper in acidic environments [4,15–22].

Quantum chemical calculations can complement the experimental investigations or even predict with confidence some experimentally unknown properties. Recently, DFT has been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor in the corrosion process [23–26]. Among the most popular electronic structure parameters are those that play a prominent role in the Hard and Soft Acid and Bases (HSAB) theory of chemical reactivity [27]. On the basis of HSAB principle, the inhibitor acts as a Lewis base while the metal acts as a Lewis acid. These parameters are then used to estimate the bonding trend of various inhibitor molecules on metal surfaces and correspondingly the corrosion inhibition effectiveness.

This present paper reports the correlation between observed inhibition efficiency of three triazole derivatives (Fig. 1) used as corrosion inhibitors with their calculated quantum chemical parameters both in the gas and aqueous environments. The experimentally determined trend of corrosion inhibition effectiveness for mild steel in 1 mol L^{-1} hydrochloric acid has been established in our previous work [16,17]. The motivation for the computational studies is not so much to provide in depth explanation of the adsorption of the derivative, but rather to give a theoretical framework in which to recognize the relative contributions of different derivative components vis-à-vis their individual adsorption mechanisms and adsorption strengths. Quantitative structure-activity relationship (QSAR) analysis [28,29] has also been used to correlate the corrosion-inhibition activity of the studied molecules with the

---

* Corresponding author. Tel./fax: +86 02365106756.
E-mail address: stzhcq@163.com (S. Zhang).

http://dx.doi.org/10.1016/j.corsci.2014.06.040
0010-938X/© 2014 Elsevier Ltd. All rights reserved.

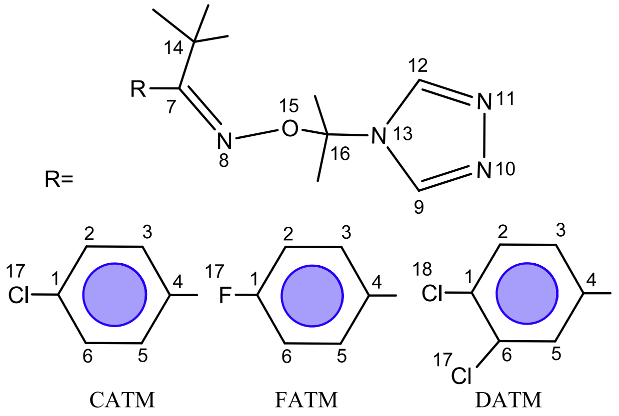

Fig. 1. Schematic representation and the atom numbering for studied triazole derivatives.

molecular structures. Recently, attention has focused on modelling the interaction of inhibitor molecules with metal surfaces and computing the interaction energies, such an approach offers the added advantage of providing important physical insights on corrosion inhibition mechanisms. Thus, the Metropolis Monte Carlo method [30] was employed to search for the adsorption configurations of the studied compounds on iron surface and to investigate the preferential adsorption sites of the studied triazole derivatives.

2. Methods and definitions

2.1. Computational details

DFT calculations were performed using Gaussian-03 software package [31]. In consideration of the hybrid B3LYP [32] functional is the most popular and reasonably accurate functional for the description of organic molecules, therefore geometry optimizations were carried out by B3LYP combination functional at the 6-31G basis set. The frequency calculations were employed to confirm the structures as minimum points in energy and achieve the relevant zero point energy. As for the description of aqueous environment, the self-consistent reaction field theory based on Tomasi's polarized continuum model (PCM) using the integral equation formalism is utilized [33].

The adsorption progress of triazole derivatives on iron surface is investigated by performing Monte Carlo simulations using adsorption locator module from Accelrys Inc. [34]. As the three kinds of Fe surfaces (1 1 0, 1 0 0, 1 1 1), Fe(1 1 1) and Fe(1 0 0) surfaces have relatively open structures while Fe(1 1 0) is a density packed surface and has the most stabilization, so we choose Fe(1 1 0) surface to simulate the adsorption process [35]. The simulation of the interaction between the triazole derivatives and the Fe(1 1 0) surface was carried out in a simulation box (2.7 × 2.7 × 4.7 nm) with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. A cutoff distance of 1.25 nm with a spline switching function was applied for the non-bond interactions (*i.e.*, van der Waals and electrostatic interactions). Using seven layers of iron atoms gives a sufficient depth that the inhibitor molecules will only be involved in non-bond interactions with iron atoms in the layers of the surface, without increasing the calculation time unreasonably. This also ensured that the depth of the surface was greater than the non-bond cutoff used in calculation. Two types of solvent layers were constructed: one consisted of 1 inhibitor molecule and 600 water molecules, and the other only consisted of 1 inhibitor molecule. A low-energy adsorption site is identified by carrying out a Monte Carlo search of the configurational space of the substrate–adsorbate system as the temperature is slowly decreased. This process is repeated to identify further local energy minima. During the course of the simulation, adsorbate molecules are randomly rotated and translated around the substrate. The configuration that results from one of these steps is accepted or rejected according to the selection rules of the Metropolis Monte Carlo method [30]. COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) was used to optimize the structures of all components of the system of interest represents a technology break-through in forcefield method [36]. It is the first *ab initio* forcefield that enables accurate and simultaneous prediction of chemical properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of state, cohesive energies, etc.) for a broad range of chemical systems.

2.2. Definitions of HSAB parameters

For an N-electron system with total energy E, qualitative chemical concepts electronegativity (χ) [37] and hardness (ξ) [38] are defined as the following first-order and second-order derivatives,

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{1}$$

$$\xi = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \tag{2}$$

where $v(r)$ and μ are the external and electronic chemical potentials, respectively. From the values of the total electronic energy, the ionization potential (I) and electron affinity (A) of the inhibitors are calculated using the following equations, and hence χ and ξ are calculated.

$$I = E_{(N-1)} - E_N \tag{3}$$

$$A = E_N - E_{(N+1)} \tag{4}$$

$$\chi = \frac{I + A}{2} \tag{5}$$

$$\xi = \frac{I - A}{2} \tag{6}$$

where $E_{(N-1)}$, $E_{(N)}$, and $E_{(N+1)}$ are the ground state energies of the system with $N-1$, N, and $N+1$ electrons respectively. The global softness (S) is simply the inverse of the global hardness: $S = 1/\xi$ [39].

As for the metal surface, the work-function, Φ, is taken as its electronegativity, whereas the chemical hardness can be neglected since ξ of bulk metals is related to the inverse of their density of states at the Fermi level-an exceedingly small number [40]. When two systems, Fe and inhibitor, are brought together, electrons will flow from lower χ (inhibitor) to higher χ (Fe), until the chemical potentials become equal. The fraction of electrons transferred (ΔN) from inhibitor molecule to the mild steel and an estimate of the initial molecule–metal interaction energy ($\Delta\psi$) are therefore given by [41]:

$$\Delta N = \frac{\chi_{\mathrm{Fe}} - \chi_{\mathrm{inh}}}{2(\xi_{\mathrm{Fe}} + \xi_{\mathrm{inh}})} = \frac{\Phi_{\mathrm{Fe}} - \chi_{\mathrm{inh}}}{2\xi_{\mathrm{inh}}} \tag{7}$$

$$\Delta\psi = -\frac{(\chi_{\mathrm{Fe}} - \chi_{\mathrm{inh}})^2}{4(\xi_{\mathrm{Fe}} + \xi_{\mathrm{inh}})} = -\frac{(\Phi_{\mathrm{Fe}} - \chi_{\mathrm{inh}})^2}{4\xi_{\mathrm{inh}}} \tag{8}$$

The electrophilicity index (φ), which measures the electrophilic power of a molecule, is defined as follows [42]

$$\varphi = \frac{\chi_{inh}^2}{4\xi_{inh}} \tag{9}$$