Corrosion Science 52 (2010) 3331–3340

Contents lists available at ScienceDirect

Corrosion Science

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

Experimental and theoretical study on the inhibition performance of triazole compounds for mild steel corrosion

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ARTICLE INFO

Article history:
Received 13 February 2010
Accepted 4 June 2010
Available online 15 June 2010

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

ABSTRACT

A relationship between quantum chemical parameters for three triazole compounds and their inhibition ability was studied using electrochemical measurements (potentiodynamic polarization and EIS), molecular dynamic method and quantum chemical calculations. Electrochemical measurements results revealed that the inhibition efficiencies increased with the concentration of inhibitors. The molecular dynamic method results showed that the higher interaction potential between the inhibitor and metal surface, the higher the inhibition efficiency. The quantum chemical calculation results showed that the triazole ring is the active site in these inhibitors and they can absorb on Fe surface by donating electrons to Fe d-orbital.

1. Introduction

Corrosion inhibitor can effectively reduce the corrosion rate of metallic materials in acid solution and has been widely applied in acidic cleanout, crude oil refiner, electrochemical and chemical etching [1]. Organic compounds, mainly containing oxygen, nitrogen and sulphur atoms and having multiple bonds, are recognized as effective inhibitors of the corrosion of many metals and alloys [2]. In different media, for a given metal, the efficiency of the inhibitor depends on the stability of the formed complex and the inhibitor molecule should have centres, which are capable of forming bonds with the metal surface via an electron transfer. Generally, a strong co-ordination bond causes higher inhibition efficiency, the inhibition increases in the sequence O < N < S < P [2]. The corrosion of mild steel in acid solutions takes place with hydrogen depolarization [3,4].

Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations [5–7]. Quantum chemical calculations have been proved to be a very powerful tool for studying the mechanism of corrosion inhibition [8]. Recently, the molecular dynamics (MD) method, often used to study the interaction of phase interfaces [9], has been applied to study the interaction between inhibitors and metal surface. Khaled [10] studied the adsorption behaviour of some guanidine derivatives on copper surfaces using molecular dynamics simulations. Xia et al. [11] investigated the adsorption behaviour of two imidazoline derivatives on Fe surface using molecular dynamics method and found that they could both adsorb on the Fe surface through the imidazoline ring and heteroatoms. In the work of Ramachandran et al. [12], the adsorptions of 1,2-dimethylimidazoline on $Fe(OH)_3(H_2O)_2$ surface and of imidazolines on Fe site of Fe_2O_3 has also been investigated using molecular dynamics simulations. Some significant results have been obtained in this investigation, which confirmed that molecular dynamics simulation was an efficient method for the study of mechanism of corrosion inhibition. However, the effect of the adsorption of electrolyte anions on metal surface has never been considered in these works. Tang et al. [13] investigated the adsorption of 2-amino-5-phenyl-1,3,4-thiadiazole and electrolyte anions on the Fe surface using molecular dynamic simulation and found that in the adsorption of sulphate ions, the system has the higher negative interaction energy comparing to the case of the adsorption of chloride ions.

The aim of this work is to correlate between the inhibition efficiencies and molecular structures of the selected triazole compounds namely, 4-amino-5-phenyl-4H-1,2,4-trizole-3-thiol (APTT), 4-amino-5-methyl-4H-1,2,4-triazole-3-thiol (AMTT) and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, 4-amino-5-hydrazine-1,2,4-triazole-3-thiol (ATTT). These molecules have been chosen because they contains one co-ordinate (=N–, $-NH_2$) and one covalent (–S –H) groups which can form a protecting film on the surface of mild steel. The inhibitory effect of the APTT on mild steel corrosion in 2.5 M H_2SO_4 has been reported in our previous work [14] while the inhibitory effects of AMTT and ATTT under the same condition were reported in this work. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were used in this study to obtain the inhibition efficiency. The quantum chemical

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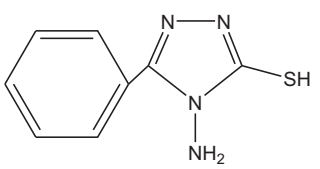
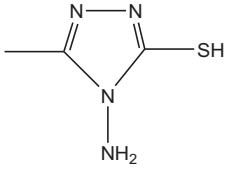
doi:10.1016/j.corsci.2010.06.002

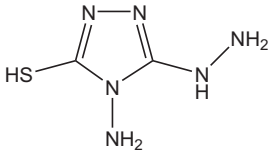
calculation and the molecular dynamics simulation method were used to elucidate the adsorption behaviour of the selected triazole compounds on the mild steel surface. The molecular structures of these triazole are presented in the following chemical formula:



APTT



AMTT



ATTT

2. Experiments and methods work

2.1. Electrochemical measurements

Electrochemical measurements were conducted to exam the inhibitory effects of AMTT and ATTT while the inhibitory effects of APTT were reported in our previous work [14]. The measurements were carried out in aerated non-stirred 2.5 M sulphuric acid solutions at a concentration range of 0.05–0.4 mM AMTT and ATTT as the corrosion inhibitors. The organic inhibitors AMTT and ATTT (Oakwood, 97%) were used as received. The rest of the materials and the cleaning procedure are same as the previously reported [14].

Electrochemical measurements were carried out on the steady-state open circuit potential (OCP) using a Gamry water-jacketed glass cell. The cell contains three electrodes, namely, the working, counter and reference electrodes, consisting of mild steel, a graphite bar and a saturated calomel electrode (SCE), respectively. Measurements were performed using the Gamry Instrument Potentiostat/Galvanostat/ZRA (REF 600) model. DC105 and EIS300 software by Gamry were used for the potentiodynamic scan and electrochemical impedance spectroscopy (EIS). The potentiodynamic current–potential curves were swept from −0.2 to +0.2 V_{SCE} at a scan rate of 0.5 mV s^{-1}. Impedance measurements were carried out using AC signals of 5-mV peak-to-peak amplitude at the open circuit potential in the frequency range of 100 kHz to 0.1 Hz. All impedance data were fitted to appropriate equivalent circuits (EC) using the Gamry Echem Analyst software. Experiments for electrochemical measurements were started about 30 min after the working electrode was immersed in the solution to allow for a stabilization of the steady-state potential.

2.2. Theoretical models and methods

The quantum chemical calculations were performed using VAMP 10.0 in Materials Studio 4.3 software from Accelrys Inc. Parametric Method (PM3), semi-empirical method was employed to obtain quantum chemical parameters and to optimize the molecule geometry [15].

The molecular dynamics (MD) simulation was performed using discover molecular dynamics module in Materials Studio 4.3 software from Accelrys Inc. Fe (1 0 0) surface was chosen for the simulation study. The MD simulation of the interaction between molecules APTT, AMTT and ATTT with Fe (1 0 0) surface was carried out in a simulation box (14.33 × 14.33 × 19.650 Å) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary boundary effects. The iron substrate with (1 0 0) plane was first optimized to minimum energy, then the addition of the electrolyte anions near to the surface followed by inhibitor molecule (Fe + anions + inhibitor) was carried out. The behaviour of the inhibitor molecule on the Fe (1 0 0) surface was simulated using the COMPASS force field (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies), which used to optimize the structures of all components of the system of interest (Fe + anions + inhibitor) and represents a technology break-through in forcefield method. COMPASS 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. It is also the first high quality forcefield to consolidate parameters of organic and inorganic materials [16].

The MD simulation was performed under 298 K, NVT ensemble, with a time step of 1 fs and the simulation time of 50 ps. The interaction energy $E_{interaction}$ between the iron surface and the inhibitor molecule through electrolyte anions (i.e., sulfate ions) was calculated as follows:

$$E_{interaction} = E_{total} - (E_{surface} + E_{ion} + E_{inhibitor}) \quad (1)$$

where E_{total} is the total energy of iron crystal together with the adsorbed anions and inhibitor molecule, $E_{surface}$, E_{ion} and $E_{inhibitor}$ are the energy of the iron crystal, sulphate ions and inhibitor molecule, respectively.

3. Results and discussion

3.1. Polarization measurements

The polarization curves of mild steel in H_2SO_4 with varying concentrations of AMTT and ATTT at 30 °C are shown in Figs. 1 and 2, respectively. Values of corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic (β_a) and cathodic (β_c) Tafel constants are listed in Table 1. These values were calculated from the Tafel fit routine provided by Gamry Echem. Analyst software, this routine uses a non-linear chi squared minimization to fit the data to the Stern-Geary equation. The inhibition efficiencies were calculated by the following expression and depicted in Table 1[2]:

$$IE\% = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \times 100 \quad (2)$$

where $i_{corr(uninh)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively.

A compound can be classified as an anodic or a cathodic type inhibitor when the change in E_{corr} value is larger than 85 mV [17]. Since the largest displacement exhibited by AMTT and ATTT are less than the borderline (Table 1), then these molecules can be considered as mixed-type inhibitors, meaning that the addition of AMTT and ATTT to H_2SO_4 solution reduces the anodic dissolution of mild steel and also retards the cathodic hydrogen evolution reaction. It was observable that the higher concentration of inhibitors shifting E_{corr} toward positive value. This indicates the inhibiting effect of AMTT and ATTT on the mild steel corrosion [18]. The values of cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) are found to change in presence of inhibitors, indicates that these inhibitors controlled both reactions. The cathodic polarization curves give rise to parallel Tafel lines with a nearly constant cathodic Tafel slopes (β_c) indicates that the addition of inhibitor to the aggressive solution does not modify the proton reduction mechanism and this reaction is activation controlled. The