Adsorption of tryptophan on iron (111): A molecular dynamics study

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ARTICLE INFO

Article history:
Received 8 December 2012
Received in revised form 26 December 2012
Accepted 27 December 2012
Available online 31 December 2012

Keywords:
Corrosion inhibition
Adsorption
Iron (111)
Tryptophan
Monte Carlo simulations

ABSTRACT

Density functional theory (DFT) calculations have been used to investigate the minimum energy structures of tryptophan adsorption on iron (111) surface. Adsorption of tryptophan molecule on iron (111) surface has been studied computationally to generate adsorption configurations and to use the force field method to obtain a ranking of the energies for each generated configuration, thereby indicating the preferred adsorption sites. In this article Monte Carlo simulation has been used to find low energy adsorption sites on both tryptophan as corrosion inhibitor and the corroding metal which simulated as iron (111) while the temperature of the whole system is gradually decreased. The results indicated that tryptophan molecules could adsorb on Fe surface through the nitrogen/oxygen atoms with the lone pair electrons in its molecule.

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1. Introduction

The use of inhibitors is one of the most practical methods to protect metals from corrosion. Unfortunately, many common corrosion inhibitors are highly toxic and health-hazardable, such as chromates [1], nitrite [2], and aromatic heterocyclic compounds[3-6]. An examination of the literature on corrosion inhibitors reveals that most organic inhibitors contain nitrogen, oxygen, sulphur and/or a de-localized pair of π-electrons through which the molecules are adsorbed on metallic surfaces and retard their corrosion [7]. Generally, inhibitor molecules may adsorb physically or chemically on the metal surface forming a layer that protect a metal from corrosion. It has been commonly accepted that an organic inhibitor usually promotes the formation of a chelate on a metal surface by transferring electrons from the organic compound to the metal and forming a coordinate covalent bond during the chemical adsorption [8]. Therefore, the power of the inhibition depends on the molecular structure of the inhibitor and the metal which is going to be protected [9]. Amino acids are attractive as corrosion inhibitors because they are relatively easy to produce with high purity at low cost [10]. Amino acids are nontoxic, biodegradable, relatively cheap and completely soluble in aqueous media. The number of publications about the inhibition effect of some amino acids on corrosion of metals increases [11-15].

Recently, the molecular dynamics (MD) method, often used to study the interaction of phase interfaces [16, 17], has been applied to research the interaction between inhibitors and metal surface. Kornherr et al. [16, 18] studied the interaction of adsorbed organosilane molecules with zinc oxide surface by molecular dynamics simulation [19]. The author has studied the adsorption behavior of some triazole derivatives on mild steel and copper surfaces [20-22] and thiazole derivatives on the mild surface using molecular dynamics simulations. Some significant results have been obtained in those investigations, which confirmed that molecular dynamics simulation was an efficient method for the study of mechanism of corrosion inhibition. However, the adsorption parameters of these inhibitors have never been considered in these works.

In the present work, tryptophan has been reported as corrosion inhibitor for mild steel in 0.5 M sulphuric acid [23]. The aim of this work is to study the adsorption of tryptophan on iron (110) surface, using molecular dynamics simulations. The objective of this theoretical study is to explain the mechanism of adsorption, and therefore offer theoretical tool regarding the understanding of mechanism of corrosion inhibition.

2. Theoretical models and methods

Accurate simulation of atomic and molecular systems generally involves the application of quantum mechanical theory. However, quantum mechanical techniques are computationally expensive and are usually only applied to small systems containing between 10 and 100 atoms, or small molecules[24]. It is not practical to model large systems such as corrosion systems containing many thousands of molecules...
in this way. Even if such a simulation were possible, in many cases much of the information generated would be discarded. This is because in simulating large systems, the goal is often to extract bulk (statistical) properties, such as diffusion coefficients or Young’s modulus, which depend on the location of the atomic nuclei or, more often, an average over a set of atomic nuclei configurations. Under these circumstances the details of electronic motion are lost in the averaging processes [24, 25].

The solvent effect on molecular structure of solute can be studied by a model, which is known as polarized continuum model (PCM) [29]. In this model, solvent is treated as a continuum dielectric medium and the solute considered as a trapped molecule in a cavity surrounded by solvent. Furthermore, the solvent dielectric constant is decreased (from about 80 to around 6 for aqueous solutions) when going from bulk of solution towards electrical double layer EDL [30]. Thus a realistic model of corrosion inhibitor must take these facts into considerations. The dielectric constant of sulphuric acid is around 100 [31], this information is used to simulate the sulphuric acid as corrosive medium.

The molecular dynamics (MD) simulations were performed using the software, Materials Studio [32]. The MD simulation of the interaction between the tryptophan inhibitor molecule and iron (111) surface was carried out in a simulation box (16.214Å × 16.214 Å × 24.1 Å) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary boundary effects[28]. The Fe (111) was first built and relaxed by minimizing its energy using molecular mechanics, then the surface area of Fe (111) was increased and its periodicity is changed by constructing a super cell, and then a vacuum slab with 15 Å thicknesses was built on the Fe (111) surface [28]. The number of layers in the structure was chosen so that the depth of the surface is greater than the non-bond cut off used in calculation. Using 4 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 structure is then converted to exhibit 3D periodicity. As 3D periodic boundary conditions are used, it is important that the size of the vacuum slab is enough (15 Å) that the non-bond calculation for the adsorbate does not interact with the periodic image of the bottom layer of atoms in the surface. After minimizing the Fe (111) surface and the amino acids molecules, the corrosion system will be built by layer builder to place the inhibitor molecules on Fe (111) surface, and the behaviors of these molecules on the Fe (111) surface were simulated using the COMPASS (condensed phase optimized molecular potentials for atomistic simulation studies) force field. Adsorption locator module in Materials Studio 6.0 [28, 33] has been used to model the adsorption of the inhibitor molecules onto Fe (111) surface and thus provide access to the energetic of the adsorption and its effects on the inhibition efficiencies of the studied amino acid [34-40]. The binding energy between the inhibitor and Fe (111) surface were calculated using the following equation [41, 42]:

\[
E_{\text{binding}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhibitor}})
\]

(1)

Where \( E_{\text{total}} \) is the total energy of the surface and inhibitor, \( E_{\text{surface}} \) is the energy of the surface without the inhibitor, and \( E_{\text{inhibitor}} \) is the energy of the inhibitor without the surface.
3. Results and discussion

3.1 Molecular dynamics simulation study

Molecule simulation methods have been successfully applied in the past to obtain the adsorption behaviors of corrosion inhibitors [41, 43–46]. Tryptophan is placed on the iron surface, optimized and then run quench molecular dynamics. Figure 1 shows the optimized structure of tryptophan. Figure 2 shows the optimization energy curves for tryptophan before putting it on the iron surface. It can be seen from Fig. 2 that tryptophan is energy optimized as well as the total energy; average total energy; van der Waals energy, electrostatic energy and intramolecular energy for tryptophan/solvent/iron surface are calculated by optimizing the whole system and are presented in Fig. 3.

![Figure 3 Optimization of the corrosion system (tryptophan/solvent/iron)](image)

The optimization process is performed by using the Adsorption locator simulation module distributed by Accelrys [47]. A Monte Carlo simulation tries to find the lowest energy for the whole system (tryptophan/solvent/iron (111)). Tryptophan is energy minimized until it satisfies certain specified criteria. The Metropolis Monte Carlo method used samples the configurations in an ensemble by generating a series of configurations, for example m, n, .... The step that transforms configuration m to n is a two-stage process [48].

First, a trial configuration is generated with probability \( \alpha_{mn} \). Then, either the proposed configuration, \( n \), is accepted with a probability \( P_{mn} \) or the original configuration, \( m \), is retained with a probability \( 1 - P_{mn} \). The overall transition probability, \( \pi_{mn} \), is thus obtained from Eq. 2 [48]:

\[
\pi_{mn} = \alpha_{mn} P_{mn}
\]

The tryptophan - iron (111) configuration are sampled from a canonical ensemble. In the canonical ensemble, the loading of all tryptophan molecules on the iron (111) substrate, as well as the temperature, are fixed.

The probability of a configuration, \( m \), in the canonical ensemble is given by equation 3 [49]:

\[
P_{m} = C e^{-\beta E_m}
\]

where \( C \) is an arbitrary normalization constant, \( \beta \) is the reciprocal temperature, and \( E_m \) is the total energy of configuration \( m \).

The reciprocal temperature is given by:

\[
\beta = \frac{1}{k_B T}
\]

where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature.

The total energy of configuration \( m \) is calculated according to the following sum [37, 48]:

\[
E_m = E_{m}^{AA} + E_{m}^{AS} + U_{m}^{A}
\]

where \( E_{m}^{AA} \) is the intermolecular energy between the asparagine molecules, \( E_{m}^{AS} \) is the interaction energy between the tryptophan molecules and the iron (111), and \( U_{m}^{A} \) is the total intramolecular energy of the tryptophan molecules. The intramolecular energy of the tryptophan is not included as its structure is fixed throughout the simulation; thus, this energy contribution is fixed and vanishes, since only energy differences play a role in Adsorption Locator calculations.

The total intramolecular energy, \( U_{m}^{A} \), is the sum of the intramolecular energy of all adsorbates of all components [37, 48]:

\[
U_{m}^{A} = \sum_{\{N\}_m} U_{int \_m}
\]

Where \( \{N\}_m \) denotes the set of adsorbate loadings of all components in configuration \( m \).

As the simulation starts with a clean iron (111) substrate, the first stage is to adsorb the specified number of tryptophan molecules. This is accomplished by a random series of insertion steps and equilibration moves (only moves that do not change the loading are permitted) until the specified loading has been reached. During this stage, only insertion steps that do not create structures with intermolecular close contacts and that pass all adsorbate location constraints are accepted [37, 48].
Table 1 The output and descriptors calculated by the Monte Carlo simulation of tryptophan confirmations on iron (111) surface

<table>
<thead>
<tr>
<th>Structures</th>
<th>Total energy</th>
<th>Adsorption energy</th>
<th>Rigid adsorption energy</th>
<th>Deformation energy</th>
<th>Tryptophan : dEad/dNi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (1 1 1) - 1</td>
<td>71.78767</td>
<td>-120.592</td>
<td>-105.157</td>
<td>-15.4355</td>
<td>-120.592</td>
</tr>
<tr>
<td>Fe (1 1 1) - 2</td>
<td>72.19276</td>
<td>-120.187</td>
<td>-103.015</td>
<td>-17.1724</td>
<td>-120.187</td>
</tr>
<tr>
<td>Fe (1 1 1) - 3</td>
<td>72.56073</td>
<td>-119.819</td>
<td>-103.766</td>
<td>-16.0533</td>
<td>-119.819</td>
</tr>
<tr>
<td>Fe (1 1 1) - 4</td>
<td>73.14195</td>
<td>-119.238</td>
<td>-101.362</td>
<td>-17.8755</td>
<td>-119.238</td>
</tr>
<tr>
<td>Fe (1 1 1) - 5</td>
<td>73.57254</td>
<td>-118.807</td>
<td>-100.833</td>
<td>-17.974</td>
<td>-118.807</td>
</tr>
<tr>
<td>Fe (1 1 1) - 6</td>
<td>74.01399</td>
<td>-118.366</td>
<td>-104.395</td>
<td>-13.9705</td>
<td>-118.366</td>
</tr>
<tr>
<td>Fe (1 1 1) - 7</td>
<td>74.30122</td>
<td>-118.078</td>
<td>-102.089</td>
<td>-15.9895</td>
<td>-118.078</td>
</tr>
<tr>
<td>Fe (1 1 1) - 8</td>
<td>74.78112</td>
<td>-117.599</td>
<td>-99.605</td>
<td>-17.9936</td>
<td>-117.599</td>
</tr>
<tr>
<td>Fe (1 1 1) - 9</td>
<td>75.13245</td>
<td>-117.247</td>
<td>-98.8002</td>
<td>-18.4471</td>
<td>-117.247</td>
</tr>
<tr>
<td>Fe (1 1 1) - 10</td>
<td>75.62692</td>
<td>-116.753</td>
<td>-99.7055</td>
<td>-17.0473</td>
<td>-116.753</td>
</tr>
</tbody>
</table>

The starting configuration will take several steps to adjust to the current temperature. A simulation is, therefore, separated into an equilibration and a production stage. The properties returned at the end of the run are based on the production stage only[48].

Figure 4 Most suitable configurations for adsorption of tryptophan on Fe (111) substrate obtained by adsorption locator module

In the equilibration and production stages of an Adsorption Locator simulation, each step starts with the selection of a step type using the weights set at the start of the run. The step type can be either a translation or a rotation. After a step type is selected, a random component is chosen and the step type is applied to a random adsorbate of that component [48]. The Metropolis Monte Carlo method is then used to decide whether to accept or reject the change [48].

The Metropolis Monte Carlo method in Adsorption Locator provides four step types for a canonical ensemble: conformer, rotation, translation, and re-growth [50]. Figure 4 shows the most suitable tryptophan conformation adsorbed on Fe (111) substrate obtained by adsorption locator module [51-53]. As can be seen from Fig. 4 both nitrogen and oxygen atoms are adsorption atoms on the iron surface. Also, the tryptophan molecule could be adsorbed on iron surface either parallel or perpendicular on the iron surface. Monte Carlo simulations enable us to calculate the adsorption energy of tryptophane as presented in Fig. 4.

Figure 5 The adsorption energy distribution of tryptophan on iron (111) surface
The binding energy of tryptophan to iron surface is calculated from equation 1 and presented in Table 1. The outputs and descriptors calculated by the Monte Carlo simulation are presented in Table 1. The parameters presented in Table 1 include total energy, in kcal mol$^{-1}$, of the tryptophan iron (111) configuration. The total energy is defined as the sum of the energies of the tryptophan, the rigid adsorption energy and the deformation energy. In this study, the energy of iron surface is taken as zero. In addition, adsorption energy in kcal mol$^{-1}$, reports energy released (or required) when the relaxed tryptophan molecules in aqueous solution are adsorbed on the iron (111) surface. The adsorption energy is defined as the sum of the rigid adsorption energy and the deformation energy for the tryptophan molecules. The rigid adsorption energy reports the energy, in kcal mol$^{-1}$, released (or required) when the unrelaxed tryptophan molecules are adsorbed on the iron surface. The deformation energy reports the energy, in kcal...
mol$^{-1}$, released when the adsorbed tryptophane molecules are relaxed on the iron surface. Table 1 shows also that (dE$_{ads}$/dN$_i$), which reports the energy, in kcal mol$^{-1}$, of iron–trypotphan configurations where one of the trypotphan molecules has been removed.

![Figure 6](image_url) Adsorption density field for tryptophan on iron (111). Figure 5 shows the adsorption energy distribution of the trypotphan molecules on Fe (111). As can be seen in Fig. 5, the adsorption energy of trypotphan reaches (-120 kcal/mol) which shows the adsorption power for trypotphan molecules on iron (111) surface.

Figure 6 shows the adsorption density field for trypotphan on iron surface. The adsorption density field presented in Fig. 6 indicates the corrosion inhibition property of trypotphan against iron corrosion.

### 4. Conclusions

Computational studies help to find the most stable inhibitor conformation and adsorption sites for a broad range of materials. This information can help to gain further insight about corrosion system, such as the most likely point of attack for corrosion on a surface, the most stable site for inhibitor adsorption, adsorption density of the inhibitor and the binding energy of the adsorbed layer.

### Acknowledgments

Authors would like to thank King Abdulaziz City for Science and Technology, KACST for the financial support of this work provided through project # AT-30-66 titled "Development of a new corrosion protection strategy for water-ammonia refrigerating systems".

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