Corrosion inhibition by L-arginine – Ce⁴⁺ system: Monte Carlo simulation study

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1. Introduction

The study of the adsorption of organic substances at electrodes, although it dates back to the early days of interfacial electrochemistry with the pioneering work of Gouy[1, 2], still attracts wide interest because of its impact on our understanding of the structure of the electrical double layer[3, 4], the kinetics of electron transfer [1, 5], the general field of corrosion (inhibition)[6], and the mechanism of electrode processes (role of intermediates)[7, 8]. Recent reviews have dealt with the adsorption of aliphatic[9] and aromatic compounds[10] at the Hg electrode, and with a comparison of different molecular models of the adsorption layer[1, 3].

The inhibiting action of organic compounds with respect to the corrosion of metals in aggressive media is most often related with their specific adsorption on the metal surface. The adsorption process, results in an effective blocking of the active sites of metal dissolution and/or hydrogen evolution thus diminishing considerably the overall corrosion rate. Hence, a correlation between the adsorption and the surface coverage with organic species is established for quite a number of cases of corrosion in inhibited acid solutions [11].

Computer modeling techniques have been successfully applied to corrosion problems [12, 13]. The application of computer modeling techniques to corrosion inhibition systems requires an understanding of the adsorption of organic compounds at the electrode-solution interface and the mathematics which govern the corrosion process. In addition, knowledge of the numerical procedures which are the basis of computer modeling techniques is necessary for accurate computational analyses. Verification of assumptions by comparison of computer analysis results with experimental or other measured data is a fundamental requirement in the creation of an accurate analysis. Simulation is a prognostic computational tool for complex scientific and engineering problems. The simplest simulation methods have been used for decades, but, with the increase in computational memory and speed simulation, have become the prevalent tool for analysis[14-17]. Understanding the fundamental interactions that bind organic molecules to the metal substrates is of crucial importance in the corrosion inhibition studies, where the competition between molecular-substrate and intermolecular interactions can lead to templated arrangements with specific spectroscopic and transport properties[18, 19]. A survey of literature indicates that only limited numbers of references are available dealing with the corrosion inhibition effect of L-arginine - cerium complex on steel surface.
In this work, the adsorption behavior of L-arginine-cerium complex at steel surface will be investigated by the molecule dynamics simulation method and density functional theory.

Figure 1 The suggested L-arginine–cerium complex structure.

2. Computational details

In this computational work the Monte Carlo simulation techniques is used to find the preferential adsorption sites on the steel surface by finding the low-energy adsorption sites on the steel surface. Materials studio 6.0, distributed by Accelrys, Inc. [20] has been used to build L-arginine–cerium complex molecule, iron surface and solvent molecules (water molecules). Molecular mechanics (force field) tools are used to investigate the simulated corrosion system [17]. The approximation used in these studies that the potential energy surface, on which the atomic nuclei move, is represented by a classical force field, which are developed by using a parameter set that derived from experiment and high level quantum mechanical calculations. Due to the presence of cerium ion in the studied complex, a universal force field has been used instead of COMPASS force field. Materials Studio software contains a full implementation of the universal force field, including bond order assignment. The Materials Studio implementation has been rigorously tested and results are in agreement with published work on this force field [21-24]. Parameter generation is based on physically realistic rules. Universal force field is a purely diagonal, harmonic force field. Bond stretching is described by a harmonic term, angle bending by a three-term Fourier cosine expansion, and torsions and inversions by cosine-Fourier expansion terms. The van der Waals interactions are described by the Lennard-Jones potential. Electrostatic interactions are described by atomic monopoles and a screened (distance-dependent) coulombic term. The universal force field types are denoted by an element name of one or two characters followed by up to three other characters: The first two characters are the element symbol (for example, N for nitrogen or Ce for titanium). The third character (if present) represents the hybridization state or geometry (for example, 1 = linear, 2 = trigonal, R = an atom involved in resonance, 3 = tetrahedral, 4 = square planar, 5 = trigonal bipyramidal, 6 = octahedral). The fourth and fifth characters (if present) indicate characteristics such as the oxidation state.

Universal force field is used for atomistic simulation studies in optimising the structures of all components of the corrosion system (iron substrate/solvent/L-arginine–cerium complex). This force field enables accurate and simultaneous prediction of chemical and condensed phase properties for a broad range of chemical systems. The first step in this computational study is the preparation of a model of molecules, which will adsorb on the surface with energy minimised structures.

Among the different steps involved in the modelling approach is the construction of the iron surface from the pure crystal, the addition of the L-arginine–cerium complex molecule near to the surface, the definition of the potentials (i.e. the force field) to study the liquid–solid interaction, followed by the geometry optimization calculation [17].

Figure 2 Forcite energy optimization for L-arginine–cerium complex.

This particular case, the use of molecular mechanics can be seen as a precursor to computationally more expensive quantum mechanical methods: Once the model has been optimised with suitable force field (Universal Force field), we will be able to simulate a substrate (iron surface) loaded with an adsorbate (L-arginine–cerium complex molecules), taking into consideration the solvent effect. This computational study aims to find low-energy adsorption sites to investigate the preferential adsorption of L-arginine–cerium complex molecule on iron surface aiming to find a relation between the effect of its molecular structure and its inhibition efficiency. To build iron surface, amorphous cell module has been used to create solvent/L-arginine–cerium complex cell on iron surface. The behaviour of the L-arginine–cerium complex on the surface was studied using molecular dynamics simulations and the COMPASS force field. The MD simulation of the interaction between the L-arginine–cerium complex molecule dissolved in aqueous solution and the iron surface (111) was carried out in a simulation box (8.1 \times 8.1 \times 24.1 \text{ nm}) with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. A cut off distance of 1.0 nm with a spline switching function was applied for the non-bond interactions,
i.e. for coulombic, van der Waals and hydrogen bond interactions. The cut off used to select the spline width, which specifies the size of the region within which nonbond interactions are splined from their full value to zero. For the actual computation of this interaction, energy charge groups are used. Cut off distance specifies the distance at which to exclude interactions from the nonbond list. The iron crystal is cleaved along with the (111) plane, thus representing the iron surface. For the MD simulation, all the spatial positions of the iron atoms in the simulation box are fixed because the thermal vibrations of the interaction with an adsorbed molecule and not in the physical behaviour of the crystal itself. The MD simulation simulates a substrate loaded with an adsorbate. 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 molecule 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 [25].

Figure 3 Most suitable configuration for adsorption of L-arginine on Fe (111) substrate obtained by adsorption locator module

The force field used is universal force field, charge is force field assigned, quality is fine and summation method is group-atom based. All structures used in this study are minimised in order to ensure that the energy results used in calculating the adsorption energy are accurate; it is critically important that when we optimise the structures, we use the same energy minimization settings as we intend to use for calculating the adsorption energy of L-arginine–cerium complex. This includes not only the force field, atomic charges, and non-bond summation methods but also the quality of the energy and geometry optimization calculations and the convergence tolerances used for the minimization. Quantum chemical calculations carried out using Dewar’s linear combinations of atomic orbitals–self-consistent field–molecular orbital (LCAO–SCF–MO) [26]. We used PM3 semi-empirical method in commercially available quantum chemical software Hyperchem, release 8.06 [27]. A full optimization of all geometrical variables without any symmetry constraint was performed at the restricted Hartree–Fock level. It develops the molecular orbitals on a valence basis set and also calculates electronic properties and the optimised geometries of the L-arginine–cerium complex molecules. As an optimization procedure, the built-in Polak–Ribiere algorithm was used [28].

3. Results and discussion

This study is a continuation of our work on the corrosion inhibition of steel in acidic and neutral medium by L-arginine [29-32] as well as a mixture of L-arginine and cerium sulphate tetrahydrate.

The inhibition efficiency of L-arginine–cerium complex was suggested in our previous[33, 34] study as follow:
The presence of cerium ions with L-arginine significantly enhances protection efficiency, which indicates there is a true synergistic inhibition effect of L-arginine and cerium ions in baseline solution. In order to explain the fact, the following synergism mechanism is suggested: Cerium ion is a member of lanthanide group in periodic table of chemical elements, and it has a many vacant orbitals (4f, 5d and 6s). L-arginine contains oxygen and nitrogen atoms with lone-pair of electrons. So, when L-arginine and cerium ions were mixed, the new complex of cerium ions–L-arginine was simply formed. The complex plays an important role in the enhancement of the protection of steel against corrosion. The suggested L-arginine–cerium complex is presented in Fig. 1. The chelation of L-arginine with cerium salts was confirmed in the literature[35].
The complex could adsorb onto steel surface by the van der Waals force to form a protective film, which considerably decrease the steel surface corrosion. In this case, L-argining molecules may play a role in bridging the access of rare earth cerium ions to the steel surface from the solution. Thus, cerium sulphate tetrahydrate and L-arginine demonstrate a strong synergistic inhibition effect for steel surface. Geometry optimization of the L-arginine–cerium complex has been performed using the Forcite module which allows performing a wide range of molecular mechanics calculations on both molecular and periodic systems using classical force field-based simulation techniques. Figure 2 shows the minimized energy distribution for L-arginine–cerium complex using forcite module in Materials studio software.
The simulated annealing task performed in this molecular dynamics study enables us to simulate the steel surface as Fe (111) loaded with a set number of L-arginine–cerium complex molecule. By searching the configurational space of the steel-
L-arginine cerium complex as the temperature is slowly decreased and then reset to the maximum through a number of temperature cycles, the low energy adsorption sites are identified. The complex molecules are confined to a defined adsorption region in the vicinity of the steel surface such that the number of L-arginine-cerium complex molecules on the surface does not change. The Metropolis Monte Carlo method is used to search for adsorption configurations. In this method, only the positions and orientations of the L-arginine-cerium complex molecules are sampled; each conformation is treated as a rigid body [30]. Geometry optimization for the L-arginine-cerium complex is based on reducing the magnitude of calculated force until they become smaller than defined convergence tolerances. The forces on an atom are calculated from the potential energy expression and will, therefore, depend on the force field that is selected [30]. Geometry optimization is carried out for the studied system using an iterative process in which the atomic coordinates are adjusted until the total energy of a structure is minimized, i.e., it corresponds to a local minimum in the potential energy surface [30].

In this computational work, the following algorithms which are available in Materials Studio software include (Steepest descent, Polak-Ribiere variant only, Quasi-Newton, Adjusted basis set Newton-Raphson, Smart) are used for geometry optimization as it used before in our previous work [30]. These algorithms are better suited to certain circumstances, for example if the structure is far from equilibrium, it is best to use steepest descent. It is, therefore, often beneficial to combine algorithms in a cascade, such that, as the potential minimum is approached, a more appropriate method is used. The Smart algorithm is a cascade of the steepest descent, ABNR, and quasi-Newton methods.

Using the Adsorption locator simulation module distributed by Accelrys, the L-arginine-cerium complex molecule – iron (111) configurations are sampled from a canonical ensemble. In the canonical ensemble, the loading of all L-arginine-cerium complex 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 1 [17, 36]:

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

(1)

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:

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

(2)

where \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature [30]. The total energy of configuration \(m\) is calculated according to the following sum:

\[
E_m = E_m^{AA} + E_m^{AB} + U_m^A
\]  

(3)

where \(E_m^{AA}\) is the intermolecular energy between the L-arginine-cerium complex molecules,
Table 1 The output and descriptors calculated by the Monte Carlo simulation of L-arginine 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>L-arginine - Ce : dEad/dNi</th>
<th>Calculated binding Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (1 1 1) - 1</td>
<td>154.43</td>
<td>-775.439</td>
<td>-11.2207</td>
<td>-764.219</td>
<td>-775.439</td>
<td>710.64</td>
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<tr>
<td>Fe (1 1 1) - 2</td>
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<td>-10.5036</td>
<td>-762.225</td>
<td>-772.728</td>
<td>702.66</td>
</tr>
<tr>
<td>Fe (1 1 1) - 3</td>
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<td>-771.919</td>
<td>-12.5705</td>
<td>-759.348</td>
<td>-771.919</td>
<td>700.56</td>
</tr>
<tr>
<td>Fe (1 1 1) - 4</td>
<td>159.558</td>
<td>-770.311</td>
<td>-11.5578</td>
<td>-758.753</td>
<td>-770.311</td>
<td>697.62</td>
</tr>
<tr>
<td>Fe (1 1 1) - 5</td>
<td>161.3331</td>
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<td>-7.97309</td>
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<tr>
<td>Fe (1 1 1) - 7</td>
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<td>-8.0281</td>
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<td>-763.062</td>
<td>661.92</td>
</tr>
</tbody>
</table>

The total intramolecular energy of the L-arginine-cerium complex, \( U^A \), is the sum of the intramolecular energy of all complex molecules of all components[30]:

\[
U^A = \sum_{\{N\}_m} U_{\text{int,ra}}
\]  

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

An Adsorption Locator simulation always starts with a steel surface. The first stage is to adsorb the specified number of L-arginine -cerium complex 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[30]. During this stage, only insertion steps that do not create structures with intermolecular close contacts and that pass all adsorbate location constraints are accepted[30].

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.

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. The Metropolis Monte Carlo method is then used to decide whether to accept or reject the change[30]. The Metropolis Monte Carlo method in Adsorption Locator provides four step types for a canonical ensemble: conformer, rotation, translation, and regrowth[37].

The adsorption density of L-arginine -cerium complex on the Fe(111) surface has been presented in Fig. 4. As can be seen from Fig. 3 and Fig. 4 that the L-arginine -cerium complex molecule shows ability to adsorb on Fe surface, and the adsorption density for a mixture of L-arginine and cerium salt is much higher than that for L-arginine alone[30].

Also, it has high binding energy to Fe surface as seen 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 substrate–adsorbate configuration[30]. The total energy is defined as the sum of the energies of the adsorbate components, the rigid adsorption energy and the deformation energy. In this study, the substrate energy (iron surface) is taken as zero. In addition, adsorption energy in kcal mol\(^{-1}\), reports energy released (or required) when the relaxed adsorbate components (L-arginine -cerium complex in H\(_2\)O) are adsorbed on the substrate. The adsorption energy is defined as the sum of the rigid adsorption energy and the deformation energy for the adsorbate components[30]. The rigid adsorption energy reports the energy, in kcal mol\(^{-1}\), released (or required) when the relaxed adsorbate components (i.e., before the geometry optimization step) are adsorbed on the substrate. The deformation energy reports the energy, in kcal mol\(^{-1}\), released when the adsorbed adsorbate components are relaxed on the substrate surface. Table 1 shows also \( (dE_{\text{ad}}/dNi) \), which reports the energy, in kcal mol\(^{-1}\), of substrate–adsorbate configurations where one of the adsorbate components has been removed. The binding energy introduced in Table 1 calculated from equation 5

\[
E_{\text{binding}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhibitor}})
\]
Where $E_{\text{total}}$ is the total energy of the surface and inhibitor, $E_{\text{surface}}$ is the energy of the Fe (111) surface without the inhibitor, and $E_{\text{inhibitor}}$ is the energy of the inhibitor without the surface.

Figure 5 The adsorption energy distribution of the adsorbate (L-arginine) on iron (111) surface.

Figure 5 shows the adsorption energy distribution of the L-arginine -cerium complex molecules on Fe (111). As can be seen in Fig. 5, the adsorption energy of L-arginine -cerium complex reaches (-770.0 Kcal mole$^{-1}$) which shows the adsorption power for L-arginine -cerium complex molecules on iron (111) surface.

4. Conclusions
Monte Carlo simulation 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. Nitrogen and cerium centers are the most likely point of attachments between L-arginine – cerium complex and the steel surface. The results indicated that the studied complex could adsorb onto steel surface by the van der Waals force to form a protective film, which considerably decrease the steel surface corrosion. In this case, L-argining molecules may play a role in bridging the access of rare earth cerium ions to the steel surface from the solution. Thus, cerium sulphate tetrahydrate and L-arginine demonstrate a strong synergistic inhibition effect for steel surface.

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