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On the nature of inhibition performance of imidazole on iron surface

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ABSTRACT

Quantum mechanical calculations based on the Density Functional Theory under periodic boundary conditions were used to construct a model for the inhibition performance of imidazole on iron surface. It is shown that, at high coverage, imidazole molecules form C–C intermolecular bonds creating a protective film, which constitutes a hydrophobic medium and, consequently, prevents adsorption of water molecules. The establishment of intermolecular bonds leads to a stabilization of the adsorption energy and this cooperative effect is the thermodynamic explanation for the film formation. These results also point out to the limitation of previous studies based on properties of isolated inhibitor molecules.

1. Introduction

Corrosion is one of the major problems encountered in the industrial application of materials. Millions of dollars are spent by the oil industry, for instance, on the prevention of corrosion process in metals. Among the procedures used to prevent corrosion, the use of inhibitors is the most common, given that it presents some advantages of economical and environmental nature, as well as great efficiency and high applicability. It is well known that organic molecules containing heteroatoms act efficiently as corrosion inhibitors [1–6]. The inhibition mechanism is not completely understood but it is commonly accepted that the inhibitor molecule forms a film that protects the metal surface. Zhang et al. [1], for instance, have shown that, by using electrochemical impedance spectroscopy (EIS), imidazole forms self-assembly films on iron surface. The inhibitor can, in principle, bind to the surface through the lone pair of electrons of the heteroatom. Side carbon chains could, in principle, help the inhibition efficiency by covering the surface more effectively. Nonetheless, even molecules without a side carbon chain show good inhibition performance, as is the case of imidazole [1,3–5]. In the latter case, adsorption could occur by the lone pair of pyrrolic nitrogen or by imidazole ring parallel to the surface. As Bhargava et al. [2] have pointed out, the nature of interaction of the inhibitor with metal surface is not yet understood at a fundamental level. Early studies were conducted on a trial and error basis, but the use of theoretical quantum and classical simulation methods can guide into an efficient choice of inhibitors [6–18].

Attempts to correlating the structure and properties of isolated molecules and their inhibition power have been reported [6–18]. They are based on properties of the isolated inhibitor molecule such as electronic density, dipole moments, atomic charges, and HOMO–LUMO gap. Although some useful information can be extracted from these analyses, they are useless to understand the inhibition mechanism itself, since the interaction with metal surface is not taken into account.

In order to cast some light on the mechanism of adsorption and possible formation of a film, studies have to be carried out on the interaction of inhibitor molecules and an explicit representation of the iron surface. Classical molecular dynamics can be used to determine the formation of self-assembled films and its dependence on temperature [16–18] but some points should be carefully considered. Inhibitor surface can form chemical bonds which have to be treated quantum mechanically. Accordingly, it is necessary to take into account specific parameters in the force field, fitted to reproduce quantum mechanical results, in order to describe this interaction properly but this point is not commonly considered in calculations. Ab initio molecular dynamics are quite expensive to treat this kind of system.

Nevertheless, several points concerning the interaction of inhibitors and metal surface can be understood by performing calculations within the framework of the density functional theory (DFT) under periodic boundary conditions. That is precisely what is done in this work.

Imidazole and its derivatives are used as corrosion inhibitors for several metals and alloys [1–5,20–26]. They are quite attractive since they represent a class of environment-friendly inhibitors, which have substituted the old fashioned and toxic materials containing arsenic and chromate [19]. The aim of the present study is to clarify the nature of the atomic interaction of imidazole molecule and metal surface and the formation of a thin film. This study was performed on the neutral form of the molecule, which was shown to be most active on inhibition by adsorption [21].

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It is shown that the formation of a film is accompanied by a stabilization of the adsorption energy due to a cooperative effect. An ultrathin film can be formed by polymerization of imidazole molecules on iron surface.

2. Calculation details

Calculations were done using periodic boundary conditions, plane wave basis set, and ultrasoft pseudopotential. The exchange and correlation functional of Perdew, Burke, and Ernzerhof [27] was used. Occupation was treated by the cold smearing technique of Marzari et al. [28]. Kinetic energy cutoff was 30 Ry. All calculations were done using Quantum-Espresso suite of programs [29]. Calculation on iron BCC bulk has been done first in order to test the pseudopotential quality. Convergence concerning cutoff energy, Monkhost–Pack sampling [30], and occupation has been tested as well. Calculation on isolated imidazole was done at the gamma point in a large cubic cell. For surface calculations, a slab model was used to construct the (001) iron surface. The supercell was composed of seven layers of iron atoms and was constructed by propagation of the original conventional cubic cell three times in the x and three times in the y directions, and a vacuum layer of 17 Å was set in the z direction, as shown in Fig. 1. The first two lowest iron layers are kept fixed during optimization. Calculations were done only at the gamma point in this latter case.

Adsorption energy is defined as

$$E_{ads} = E_{n-imz/slab} - nE_{imz} - E_{slab}$$

where E_{ads} is the calculated adsorption energy, $E_{n\text{-}imz/slab}$ is the energy of the adsorbed system (n-imidazole molecules + slab), nE_{imz} is the energy of n isolated imidazole molecules in gas phase, and E_{slab} is the slab energy. With this definition, a negative E_{ads} corresponds to a stable adsorption.

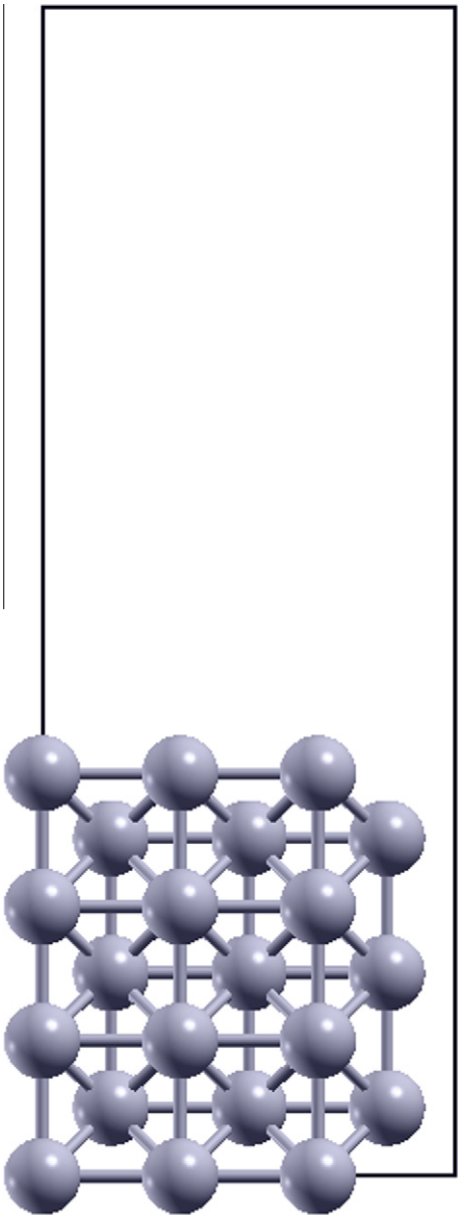

Fig. 1. Side view of the slab model for (001) Fe surface calculation. The unit cell is composed of seven Fe atom layers, each one consisting of nine atoms, and a vacuum layer of 17 Å.

3. Results and discussion

3.1. Bulk iron

Ground state properties of Fe crystal have been a challenge to theoretical approach. For example, it has been shown [33] that the correct description of magnetization can only be made by Generalized Gradient Approximation (GGA) approach to DFT. In order to verify the quality of the pseudopotential, calculation has been performed on bulk properties of BCC iron first. The results for lattice constant and magnetization are 2.82 Å and 2.16 bohr.mag/cell, in a $7 \times 7 \times 7$ Monkhost–Pack sampling, which should be compared to the experimental values 2.86 Å and 2.22 bohr.mag/cell [31,32]. Lattice constant and magnetization are in good agreement with experimental values. From this, the surface calculation was carried out.

3.2. Imidazole adsorption

The adsorption of a single imidazole molecule was done in two ways, by the nitrogen atom with the molecule adopting a geometry perpendicular to the surface or by setting the five-member ring parallel to the surface, as shown in Figs. 2 and 3. Adsorption energies for one imidazole molecule are given in Table 1.

The preferred adsorption site for perpendicular adsorption is atop and for parallel is hollow, but the difference between them is less than a 1.5 kJ/mole which is on the order of magnitude of the error due to the method. So, at this step, one cannot state which is the preferred form of adsorption and, in principle, they are interconvertible.

The main goal of this work is to verify whether corrosion inhibition could be understood by ab initio calculations. In order to accomplish this, it is important to see what happens with the increase in adsorption coverage. In Fig. 4, one can find the model for adsorption of four imidazole molecules per unit cell. The multiple adsorptions and, consequently, the formation of a layer are quite favorable. The adsorption energy of −765.63 kJ/mol is lower than that of a single imidazole molecule, i.e., −569.36 kJ/mol (Table 1). These results indicate the occurrence of a cooperative effect during imidazole adsorption, which leads to the formation of a thin film. The nature of the film can be rationalized by considering the process of its formation as the breaking of double bonds on the imidazole rings and formation of C–C sigma bonds between different imidazole molecules, which are not planar anymore. The adsorbed species are quite different from that in the gas phase.

For the most stable structure with four imidazole molecules, shown in Fig. 4, the molecular surface was calculated by adding