

탄소강 부식 억제제로서 알칸 티올의 Ab-initio DFT 모델링

Ab-initio DFT Modeling of Alkanethiols as Carbon Steel Corrosion Inhibitors

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Abstract

In the present work, we simulated and explained the bonding of three alkanethiols - hexanethiol (HT), decanethiol (DT), and 11-mercaptoundecanoic acid (MDA) - with Fe(110) surface and Fe₂ clusters using Density Functional Theory (DFT) to probe the corrosion inhibition mechanisms. The interaction energies computed from periodic DFT calculations successfully predicted the experimental inhibition performance. We have found strong covalent bond formation between S(thiol) and Fe-atoms in both approaches, further confirmed by the projected density of states and electron density difference. Besides, natural bond orbital (NBO) charge distribution showed that DT had stronger electron-donation and back-donation synergic interactions with Fe-atoms.

키 워 드: 강철, 모델링 연구, 인터페이스, 산 억제, 중립 억제

Keywords : steel, modelling studies, interfaces, acid inhibition, neutral inhibition

1. Introduction

Corrosion of iron alloys remains among the most challenging problems in almost all industrial sectors because of tremendous financial loss and security threats every year. The use of organic corrosion inhibitors is one of the best and simplest strategy to protect metals against corrosion, especially in acidic medium. These chemical species adsorb on the metal surface, forming a protective layer that prevents the attack of aggressive particles.

Alkanethiols are a class of thiol-based compounds that possess high affinity toward metals. We use herein DFT-based computations to probe Hexanethiol, decanethiol, and 11-mercaptoundecanoic acid interactions with Fe(110)surface. Furthermore, Natural Bond Orbital (NBO) analysis of alkanethiols - Fe₂ was performed to understand the charge distribution between the filled and vacant orbitals in inhibitor-iron systems.

2. Materials and Method

All first-principles calculations were performed in the framework of DFT with the generalized gradient approximation in the Perdew, Burke, and Ernzerhof (GGA-PBE) for describing the exchange-correlation energy of interacting electrons. The ionic cores were described using Vanderbilt ultra-soft pseudo-potentials. A kinetic energy cut-off of 300 eV was set for all the calculations. Van der Waal's (vdW) forces were included through the DFT-D3 parametrization of Grimme. Sampling in the Brillouin zone was performed using a Monkhorst-Pack grid of 8×8×8 for bulk lattice optimization of the body-centered cubic (bcc) iron. This procedure reproduced a lattice constant equal to 2.864 Å, close to the experimental one of 2.866 Å. For the interaction between alkanethiols and iron surface, bulk supercell was cleaved along the (110) plane consisting of four layers. Then, a (5×5)-supercell was created with a vacuum slab of 20 Å in the z-direction to reduce the spurious interactions between the neighboring slabs. The DFT CASTEP package implemented in Materials Studio was used for all calculations.

3. Results and Discussion

Upon adsorption, the sulfur atom of alkanethiols is bonded to one (parallel geometry) and two adjacent Fe atoms (Fe-S-Fe) (perpendicular geometry) with bond-lengths of dS-Fe between 2.185 and 2.303 Å, which are shorter than

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the sum of the covalent radii for sulfur and iron atoms ($r_S + r_{Fe} = 1.05 \text{ \AA} + 1.32 \text{ \AA} = 2.37 \text{ \AA}$). It signifies that the thiol group chemisorbed on the iron surface via the formation of covalent bonds, as shown in Figure 1(b) and (c).

Electron density difference plots in Figure 1 (c) and (d) show a significant electron density buildup in the Fe-S bonds' direction. The iso-surfaces show a substantial electron depletion above the S atom, which tends to donate its electrons to iron atoms. The Projected densities of states (PDOSs) for the most stable configurations shows decreased molecular peaks after adsorption, indicating strong binding, and that the charge has been transferred to the iron atoms. Upon the adsorption of alkanethiols and formation of Fe-S covalent bonds, the s and p electronic states density peaks broadened and extend to low energy regions noticeably.

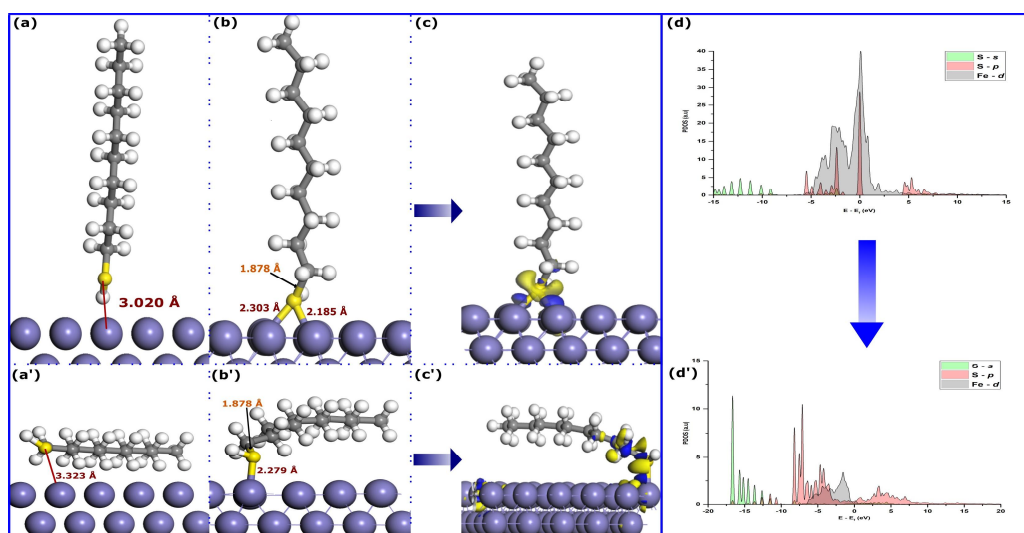


Figure 1. Initial (a) perpendicular and (a') parallel adsorption configurations of DT on Fe(110) surface; optimized (b) perpendicular and (b') parallel adsorption configurations of DT on Fe(110) surface; (c) and (c') electron density difference plots for optimized perpendicular and parallel adsorption geometries, respectively; (d) and (d') PDOS for DT molecule before and after adsorption on Fe(110) surface.

4. Conclusion

The adsorption characteristics of three alkanethiols on Fe(110) surface and Fe₂ iron clusters were investigated using periodic and cluster DFT calculations, respectively. Evidences from bond lengths, PDOS, and electronic density difference confirmed that, upon adsorption of alkanethiols on iron surfaces, a robust covalent S(thiol)-Fe bond was formed.

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