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Unravelling the Corrosion Inhibition Mechanism of Carboxymethyl Cellulose on Iron Surface Using DFT

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ABSTRACT

The use of corrosion inhibitors (CI's) is one of the most effective and economical means to combat corrosion. Owing to increased environmental concerns, there is a need for environmentally benign and green CI's. In this regard, although there have been several experimental studies reporting polysaccharides as promising green CI's for steels in various acidic media, the underlying mechanisms are not well understood. Molecular modeling methods based on the density fuctional theory (DFT) have been mostly limited to the computation of quantum chemical descriptors like the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the isolated molecule. We have employed DFT to model the adsorption of carboxymethyl cellulose (CMC) – an experimentally known polysaccharide CI for steels, with the Fe (001) surface. From the computed interaction energies, optimized structures and electron density difference plots, it can be inferred that the interactions are governed by chemical interactions between O-atoms of the OH-functional groups in CMC (rather than the hetero O-atoms as has been hypothesized earlier for another polysaccharide, guar gum) and the surface Fe-atoms. Thus, our computations provide important insights into the nature of CMC-Fe surface interactions which are difficult to gain experimentally. This approach, when used in conjunction with experiments, can help in the design and development of novel molecules for use as green CI's for metal surfaces.

Keywords: DFT, Corrosion inhibitor, CMC, Fe (001), Interaction energy and electron density difference

INTRODUCTION

The properties of metals and alloys deteriorate when they come in contact with corrosive elements present in the environment by the process commonly known as corrosion. Aggressive acids (e.g. H_2SO_4, HCl) are widely used in many industrial processes such as acid pickling, acid cleaning, acid descaling and oil well acidizing etc. [1-2] These acids enhance metal dissolution thus causing early failure of the metals.

Many organic compounds containing polar functional groups in their molecules have been tested for corrosion prevention of iron/steel in various acidic media. [3-5] These inhibitors reduce the corrosion rate by adsorption of molecule onto the metal surface and decreasing the diffusion rate of corrosive element onto the metal surface.[6] The compounds containing heteroatoms O, N, S and P have been found to act as CI's and inhibition efficiency follows the sequence: O< N< S< P. [6-8] Most of the organic and inorganic compounds are toxic, costly, environmentally unfriendly and non-biodegradable which have prompted researchers to find new CI's that are economically and environmentally favorable.

Several experimental electrochemical techniques have been reported in literature to study the inhibition efficiency duly accompanied by surface analysis method such as cyclic voltammetry, scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, FTIR analysis, scanning tunneling microscopy etc. [9-13] Chitosan, starch, guar gum, carboxymethyl starch, pectin, hydroxyl-ethyl cellulose and gellan gum etc. have been studied comprehensively as CI's for different metals and alloys (Aluminum, copper, mild steel, cast iron, carbon steel and 304 steel) in acidic medium. [14-16] But the underlying mechanisms of inhibitor-surface bonding are not well understood. Thus molecular modeling based approaches such as density functional theory (DFT) can play an important role in understanding the nature of inhibitor-metal surface interactions and thus aid selection and design of new molecules as CI's. It is possible to predict adsorption related electronic properties, adsorption geometries and energies from electronic structure calculation methodology like DFT. In the present study we have applied DFT to study the interaction mechanisms of carboxymethyl cellulose (CMC) with the Fe surface. It has been experimentally found that CMC exhibits a maximum inhibition efficiency of 78% at a concentration of 0.04% (wt. %) in 1 M HCl at room temperature for mild steel[16] while for carbon steel it shows 98% inhibition efficiency in ground water at 250 ppm concentration in presence of 50 ppm concentration of Zn^{+2} [17] Three different conformations of CMC on Fe (001) surface were optimized and the corresponding interaction energies were calculated.

COMPUTATIONAL METHODOLOGY

Fe (001) surface modeling

A (5x4)-supercell containing 100 Fe-atoms was created in Materials Studio 4.1[18] and optimized using PWscf code contained within the Quantum Espresso-5.0.2 package[19]. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhoff was used for the exchange correlation functional. [20] Rappe's ultrasoft pseudopotentials were employed for describing the ionic cores. [21] The Kohn-Sham wave functions were expanded using plane wave basis sets. A kinetic energy cut-off of 35 Ry (476.2 eV) and charge-density cut-off of 300 Ry (4081.7 eV) were used in this work. In order to avoid the interaction between the adjacent periodic supercells, a vacuum of at-least 10 Å was ensured between the adjacent supercells along the z-direction. The Broullion zone integration was limited to gamma point because of the large system size. The Fermi-surface was treated using a Methfessel-Paxton smearing technique with a smearing parameter of 0.025 Ry. [22] The structural relaxations have been performed using conjugate gradient algorithm with a force convergence cut-off of 0.01 eV/bohr per atom.

Isolated molecule: CMC dimer

CMC is a polysaccharide derived from cellulose with carboxymethyl groups bound to some of the hydroxyl groups of the glucopyranose monomers. In our computations, we have modeled CMC using two monomeric units. The starting conformation of the CMC dimer created using the graphical visualizer of Materials Studio-4.1 and optimized using PWscf is shown in Figure 1.

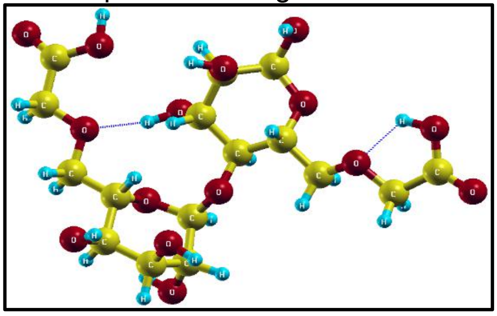


Figure 1 – Optimized chemical structure of carboxymethyl cellulose dimer. (Atoms legend: aqua = H, yellow = C, dark red = O, violet = Fe)

Modeling of the Fe – CMC Complex System

Three different conformations of CMC on Fe (001) surface were investigated (Figure 2). The vertical conformation was created in such a way that one of the doubly bonded O atoms of carboxymethyl group and one of the O atoms of the hydroxyl group are in close proximity with Fe atoms of the surface [Figure 2 (a)]. On the other hand, the horizontal conformations were created so as to facilitate maximum interactions with the Fe surface (Figure 2 (b, c)).

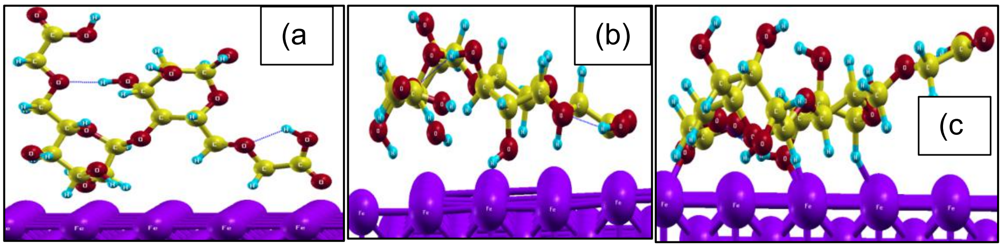


Figure 2 – Initial adsorption geometries of CMC on Fe (0 0 1) surface. (Atom legends: aqua = H, yellow = C, dark red = O, violet = Fe). Conformation 1, 2 and 3 corresponds to Figure 2 (a), 2 (b) and 2 (c)

RESULTS

Molecular descriptors

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the geometry optimized CMC are shown in Figure 3. The computed values were found to be E_{HOMO} = -5.1669 eV, E_{LUMO} = -0.9696 eV and the energy gap $E_{LUMO-HOMO}$ = 4.1973 eV. The energy band gap signifies the amount of energy required to remove the electron from the last occupied orbital. The energy gap for CMC is lower than that of several other carbohydrates. [23] As the energy gap decreases, the reactivity of the molecule increases resulting in higher inhibition efficiency. [24-25] Thus it can be interpreted that CMC is a better CI compared to other carbohydrates.

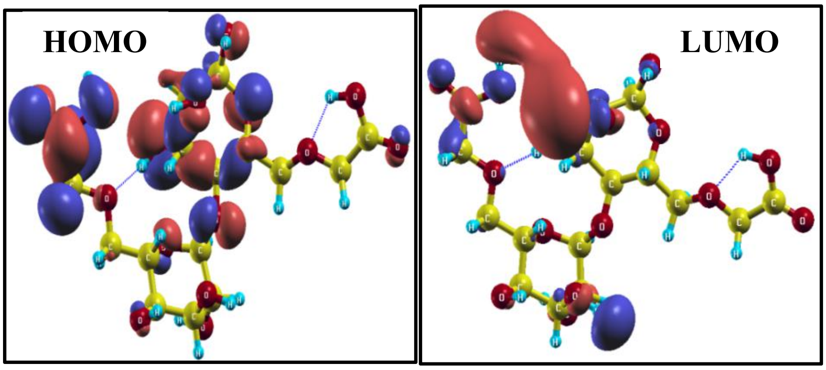


Figure 3 – HOMO-LUMO plot for optimized CMC molecule. (Atoms legend: aqua = H, yellow = C, dark red = O, violet = Fe)

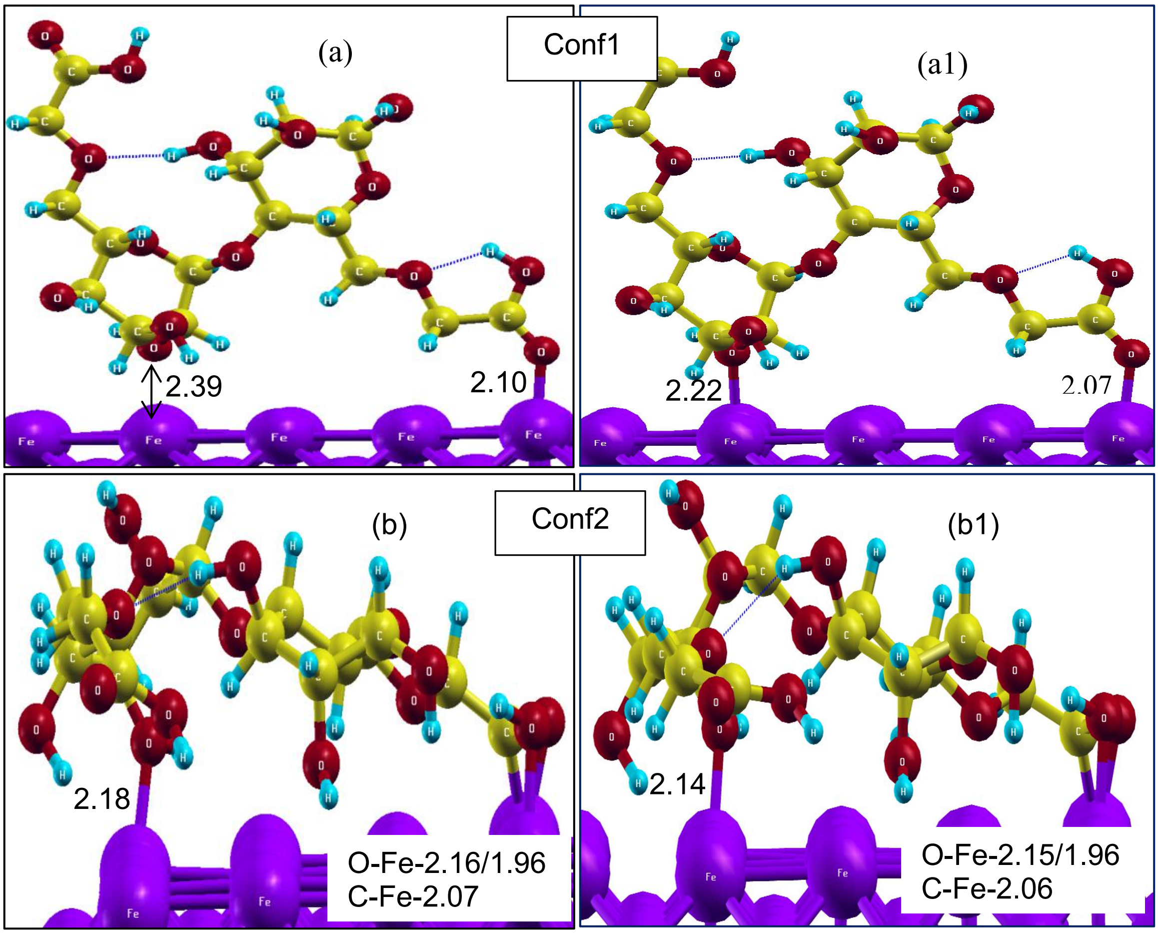
Optimized Adsorption Geometry and Interaction Energy

Three different adsorption geometries have been explored in order to find out the most stable adsorption geometry for covalent interactions between CMC and Fe (001) surface. Figure 4 shows the key variation in the adsorption geometries considered for optimization. In the perpendicular adsorption geometry the inhibitor molecule (CMC) is oriented perpendicular to the Fe (001) surface whereas in the parallel adsorption geometries the inhibitor molecule is aligned parallel to the Fe (001) surface.

In the perpendicular adsorption geometry (Conf1), the computed interaction energy was ~-48.1 kcal/mol; whereas, in the parallel adsorption geometries (Conf2 & 3) the interaction energies were found to be ~ -54.6 and -46.6 kcal/mol, respectively. The optimized geometries indicate that there is a chemical interaction between CMC molecule and Fe atoms of the surface. The average bond length between the adsorbate oxygen and the surface Fe atoms is 2.09 Å which is close to the covalent radii of Fe and O, ~2.20 Å.

To further investigate the effect of van der Waal's dispersion interactions on the interaction mechanisms, the optimization was carried out with inclusion of dispersion forces. The dispersion corrections enhance the molecular adsorption bonding which results in increase in the interaction energies and decrease in the equilibrium distance between the molecule and the surface (Figure 4, Table 1).

As indicated in Table 1, the interaction energies are significantly higher in case of the parallel adsorption geometry (Conf2 & Conf3) than the perpendicular one (Conf1) owing to the strong interaction between the oxygen and carbon atoms of the inhibitor molecule and Fe atoms of the surface. Among the three adsorption geometries, Conf2 was found to be the most favored energetically while conf1 is the least favored.



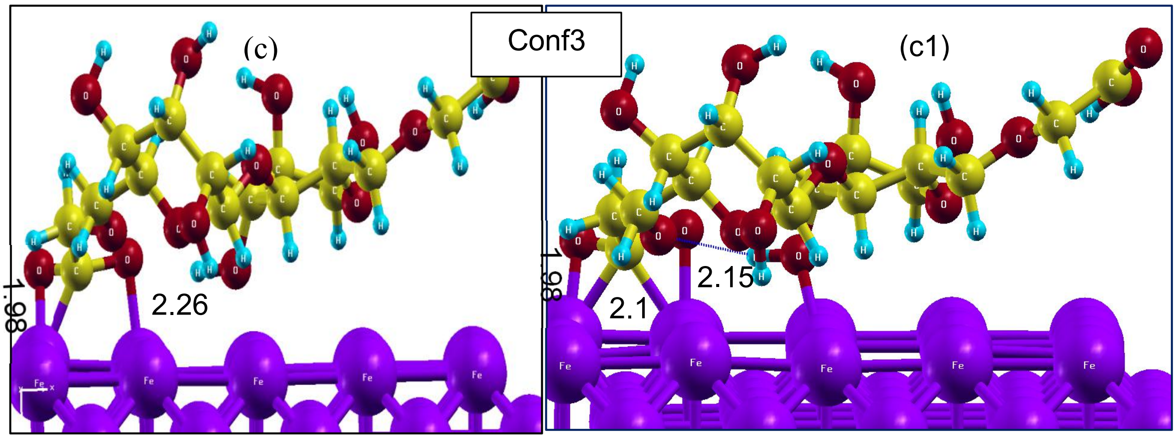


Figure 4 - Optimized adsorption geometries of CMC on Fe (001) surface. Figure a, b, c show optimized geometries without dispersion forces and Figure a1, b1, c1 show optimized geometries with dispersion forces. The numbers indicate the distance between the atoms in Å. (Atoms legend: aqua = H, yellow = C, dark red = O, violet = Fe)

Table 1 - Interaction energy of CMC molecule with Fe (001) without (DFT) and with (DFT+D) dispersion forces.

Molecule	Conformation	Interaction energy (kcal/mol)		% Change
		DFT	DFT+D	
CMC	1	-48.1	-77.6	61.51
	2	-54.6	-124.3	127.4
	3	-46.6	-102.8	120.18

Electronic Charge Density Difference

In order to investigate the changes in electronic structure as a result of CMC adsorption on Fe (001) surface, the plots for the electronic density difference, Δρ(r) were calculated by using the following expressions:

$$\Delta\rho(r) = \rho_{total}(r) - \rho_{surface}(r) - \rho_{inhibitor}(r)$$

Where ρ_{total}(r), $\rho_{surface}$ (r) and $\rho_{inhibitor}$ (r) are electron densities of Fe-CMC complex, Fe (001) surface and isolated CMC molecule, respectively.

The electronic density difference plots with an isosurface value of 0.003 e/Å^3 for all the three conformations are shown in Figure 5. The brown regions represent charge accumulation while the blue regions indicate charge depletion. The formation of O-Fe and C-Fe bonds is clearly shown by charge redistribution between the corresponding O, C and surface Fe atoms. The charge flow occurs from the bonded atoms (O-Fe, C-Fe) towards the centre of the O-Fe and C-Fe bonds. The distribution of charge is similar for all the three conformations hence the adsorption strength is governed by number of bonds formed between the inhibitor molecule and the metal surface. Thus by looking into the charge distribution between CMC and Fe (001), it can be interpreted that conformation 2 is most favored.

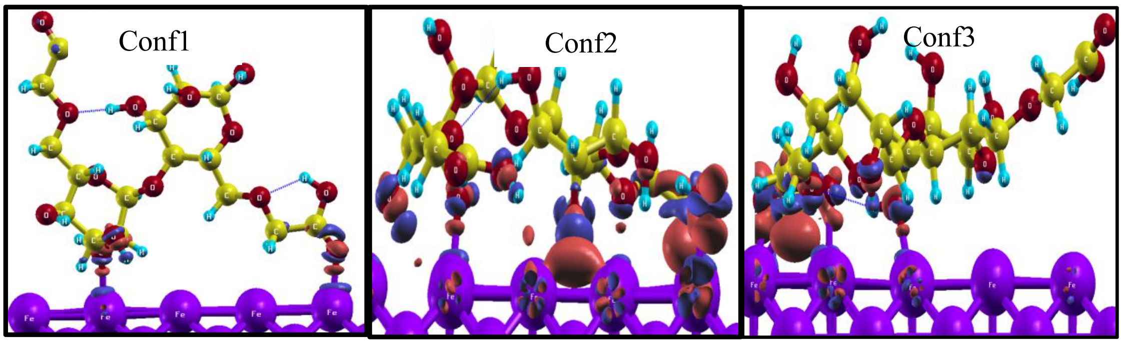


Figure 5 – Electron density difference plots for optimized adsorption geometries of CMC-Fe (001). (Atom legends: aqua = H, yellow = C, dark red = O, violet = Fe)

CONCLUSIONS

The adsorption binding of inhibitor molecule CMC to Fe (001) surface was investigated by means of DFT calculations. The lower HOMO-LUMO gap of CMC from other carbohydrates indicates that CMC might be a better inhibitor. The computed interaction energies for CMC was found to be sensitive to initial conformation and also strongly influenced by the inclusion of dispersion corrections in the calculations. Three different conformations of CMC on Fe (001) surface were investigated and conformation 2 was found to be the most energetically favored adsorption mechanism. Without dispersion corrections, the interaction energies fall in between -45 to -55 kcal/mol while inclusion of dispersion corrections leads to increased values in the range -75 to -125 kcal/mol for. The computed O-Fe and C-Fe bond distances and electron density difference plots indicate chemisorption between CMC and Fe (001) surface. Thus, our computations give important insights into the nature of CMC-Fe surface interactions which is difficult to gain through experimental techniques. Our approach, when used in conjunction with experiments, can help in the design and development of novel molecules for use as green corrosion inhibitors for metal surfaces.

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