

Understanding the Adsorption Morphologies of Quaternary Ammonium-based Corrosion Inhibitors at Metal-Water Interfaces via Molecular Simulations

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ABSTRACT

In this work, we perform all-atom molecular dynamics simulations to study the adsorption morphology of alkyldimethylbenzyl ammonium bromides (henceforth referred as q-c molecules). Our simulations reveal that q-c12 molecules (inhibitor molecules with 12 carbon atom long tail) adsorb in an ordered, standing-up orientation on the metal surface, whereas the adsorption of q-c4 molecules (inhibitor molecule with 4 carbon atom long tail) is rather disordered. Our free energy calculations further support that because of an ordered adsorption, a greater number of q-c12 molecules adsorb onto the surface as compared to the q-c4 molecules.

Key words: corrosion inhibitors, adsorption morphology, free energy, molecular simulations

INTRODUCTION

Use of corrosion inhibitor molecules is an effective way to control internal corrosion of oil and gas pipelines. The corrosion inhibitor molecules adsorb onto the metal surface and form a barrier for the ingress of water molecules to the surface. Prediction of adsorption morphology of corrosion inhibitor molecules is an important yet a challenging task because of our inability to examine the atomic species with microscopy and spectroscopy techniques.¹ Details such as thickness, deposited mass of adsorbed inhibitor film have been estimated from AFM and EQCM measurements, respectively.²⁻³ However, the adsorption morphology of inhibitor molecules have only been hypothesized. Researchers have predicted several adsorption morphologies of quaternary ammonium molecules, such as self-assembled monolayer (SAM), bilayer, micellar state etc.^{2, 4-6}

In this work, we study the adsorption morphology of corrosion inhibitors via molecular dynamics (MD) simulations. We choose alkyldimethylbenzyl ammonium bromide molecules of two different alkyl tail lengths to understand their adsorption morphologies on metal-water interfaces. These are quaternary ammonium molecules, which are widely used in oil and gas industries.⁷⁻⁸

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In this work, we have reviewed some of our previously published results on straightforward molecular dynamics (MD) simulations of these molecules on metal surface.⁹ However, a complete understanding of stable adsorption morphology is possible only by performing free energy calculations of different adsorption morphologies. These calculations can be performed by employing advanced sampling techniques in MD simulations. We, therefore, report here our novel free energy methodology to enable sampling of high-density adsorption morphologies which are not obtained in straightforward MD simulations.

SIMULATION METHODOLOGY

In MD simulations of inhibitor molecules, the molecules are initially placed in an aqueous medium near the metal surface. Simulations are then performed by integrating classical equations of motion for all the species in the simulation box. Each atom/ion moves according to the forces acting on it from the surrounding species. The forces are the result of interaction potentials which are mainly Van der Waals potential between non-ionic species and Coulombic potential between the ionic species. The interaction potential parameters are obtained by matching thermodynamic properties from simulations with the properties obtained from density functional theory (DFT) calculations and experiments. The structure of the molecules studied in this work is shown in Figure 1.

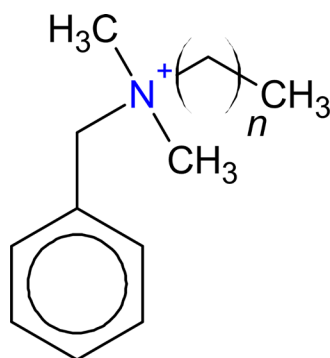


Figure 1: Structure of alkyldimethylbenzyl ammonium molecule employed in this study. The subscript n corresponds to the number of CH_2 groups in the alkyl tail of the molecule. q-c4 and q-c12 have 3 and 11 number of CH_2 groups in their alkyl tails.

Interaction Potential Models. We perform fully atomistic MD simulations of 42 inhibitor molecules in 1502 water molecules near the metal surface.⁹ The inhibitor molecules are charged and therefore, an equal number of bromide ions are introduced in the simulation box as the counter-ions to keep the system charge neutral. The metal surface is represented by a gold lattice which consists of six layers of gold atoms in (111) plane, with a lattice constant of 4.08 Å. The interaction between the species is modeled via the Lennard-Jones and Coulombic potentials. The potential parameters for inhibitor molecules are taken from the General Amber Force Field (GAFF).¹⁰ GAUSSIAN-16 program is used to obtain partial charges on the inhibitor molecules using DFT level theory of B3LYP and 6-31G (d,p) orbital basis sets.¹¹ Water molecules are modeled via the Single Point Charge Enhanced (SPC/E) water model.¹² The parameters for bromide ions are taken from the Joung-Cheatham's model.¹³ Gold is chosen for adsorption study because of the availability of its accurate interface field from Heinz's model.¹⁴ Moreover, EQCM studies have shown a similar adsorption behavior of corrosion inhibitor molecules on gold and iron surfaces.³ We believe that this is attributed to their similar polarizability and strong affinity for the species.

Simulation Box Setup. The simulation box is comprised of a metal slab at one face which is in contact with the aqueous column comprising of inhibitor molecules and the counter-ions (Figure 2 (a/b)). The size of the simulation box is 34.62 Å x 34.98 Å x 80 Å.⁹ Periodic boundary conditions are employed in X and

Y directions. The Z direction is non-periodic because of the presence of metal slab and a vapor space above the aqueous column. The length of the water column is ~ 60 Å. Simulations are performed in the isothermal-isochoric (NVT) ensemble at a temperature of $T = 300$ K.⁹ A vapor space of ~ 20 Å is kept above the aqueous column so as to keep the system pressure at the saturation pressure corresponding to $T = 300$ K.¹⁵ LAMMPS, a molecular dynamics simulator package, is used to perform all the simulations.¹⁶ Simulations are run sufficiently long (773 ns for q-c4 molecules and 580 ns for q-c12 molecules) to ensure that the system reaches equilibrium.⁹ At equilibrium, the distribution/density profiles of inhibitor molecules, counter-ions and water molecules from the metal surface do not change with time.

RESULTS

MD Simulations of Inhibitor Molecules at Metal-Water Interfaces

We arrange inhibitor molecules in a SAM configuration at metal-water interface following the previous works¹⁷⁻¹⁸ and perform MD simulations to see how the molecules re-arrange to attain a more stable configuration.⁹ Figure 2 shows the configuration of the molecules at $t = 0$ ns and $t = 773$ ns / 580 ns for q-c4 / q-c12 molecules, respectively.

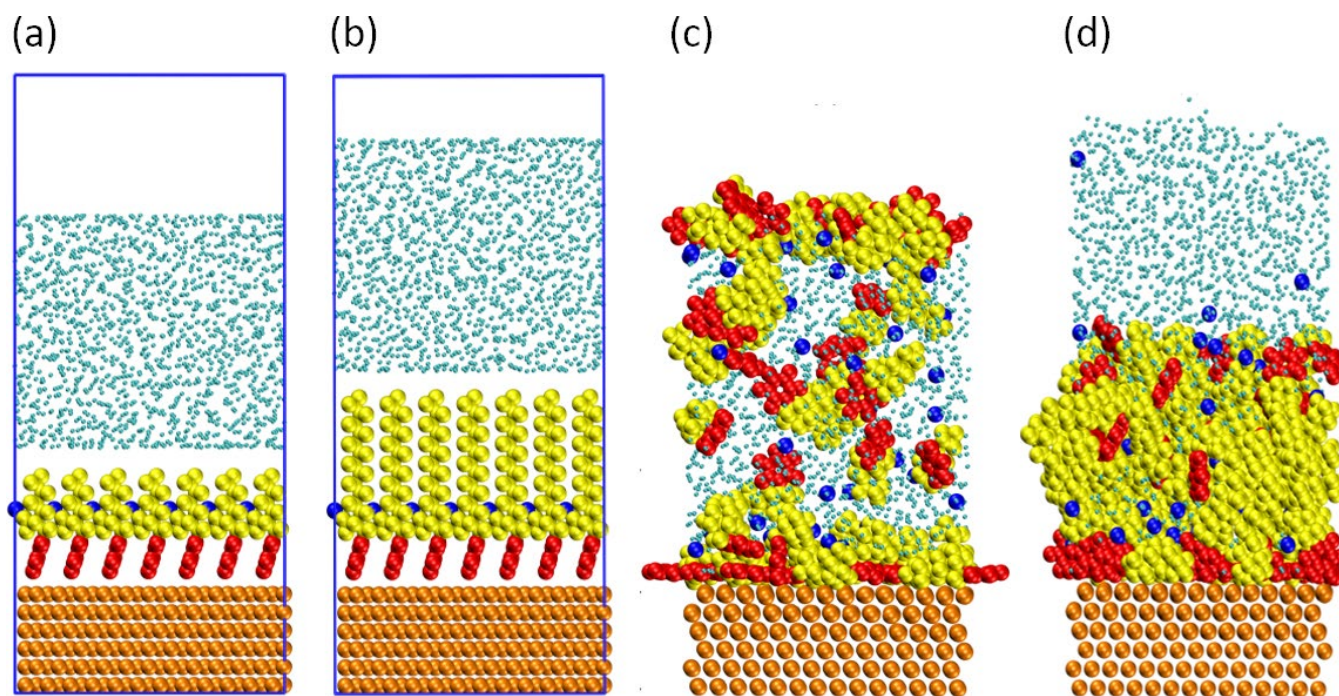


Figure 2: Snapshots of configuration of (a) q-c4 molecules at $t = 0$ ns, (b) q-c12 molecules at $t = 0$ ns, (c) q-c4 molecules at $t = 773$ ns, and (d) q-c12 molecules at $t = 580$ ns. Red beads represent aromatic rings, yellow beads represent alkyl tails, blue beads represent bromides, orange beads represent gold atoms and cyan beads represent water molecules. Cyan beads are shown relatively smaller in size for clarity purposes. Molecules are considered adsorbed when their center-of-mass (COM) lie within one molecular length from the metal surface.

The adsorption morphology after the simulation shows that the molecules rearrange on the surface and attain a configuration in which q-c12 molecules look much more packed than those of q-c4 molecules. q-c12 molecules remain adsorbed on the surface whereas a good fraction of q-c4 molecules diffuse into the bulk aqueous phase.⁹ This indicates that for the same number of molecules, adsorption of q-c12 molecules is more favorable than q-c4 molecules.