Molecular Simulations to Study Adsorption and Self-Assembly of Corrosion Inhibitors on Metal-Water Interfaces

BACKGROUND

The Institute of Corrosion and Multiphase Technology (ICMT) of Ohio University is a pioneer research institute in the world involved in solving the complexities of corrosion inhibition in oil and gas pipelines. Corrosion is a major concern of the oil and gas industry, costing more than $7 billion per year in maintenance, and responsible for many life-threatening and environmentally damaging hazards[1]. A popular and cost-effective methodology to inhibit corrosion in oil and gas pipelines is to inject certain surfactant molecules in parts-per-million levels in the oil stream[2]. These surfactant molecules, called corrosion inhibitors, form an adsorbed film of molecular dimensions on metal surfaces to retard corrosion[3]. Supposedly, corrosion inhibitor molecules organize or self-assemble at the metal-water interface to form a protective film[4]. As one would imagine, depositing/adsorbing a well-organized film of molecular thickness on metal surfaces, especially in field conditions, is a grand challenge for the industry. Not surprisingly, it is still an imperfect technology and considerable effort is being invested to design better corrosion inhibitor molecules[2]. So far, research in this area has primarily focused on applying experimental methodologies to find better corrosion inhibitors. In my PhD research, I approach this problem from a radically different dimension. I am using computer simulations to examine behavior of corrosion inhibitor molecules near metal surfaces. While previous researchers have focused on studying interactions of a single molecule with metal using computational methods[5], my research is unique in the way that I am examining how swarms of corrosion inhibitor molecules adsorb, self-assemble and aggregate on metal-water interfaces. I am systematically varying the chemistry of these molecules in my simulations to record corresponding changes in the behavior of these molecules near metal-water interfaces. By approaching this problem using molecular simulations, fundamental relationships between molecular chemistry and adsorption behavior will be developed. Based on these insights, optimum corrosion inhibitor molecules will be identified. I am currently in the third year of my PhD program. My first research study on this work has been published in the Journal of Physical Chemistry B[6]. As I will briefly discuss, my first research study has revealed interesting adsorption mechanisms of corrosion inhibitor molecules which stand to challenge conventional ideas. An advantage of being a student at Ohio University is that my molecular simulation results can be verified by experimental techniques available at the ICMT.

RESULTS FROM MY PREVIOUS STUDY

Metal surfaces are known to have a strong affinity for polar groups. Polar functional groups are groups which have an easily polarizable electron cloud or have lone pair of electrons, such as aromatic rings, alcohols, groups containing nitrogen, oxygen or phosphorus atoms, etc. It is generally presumed that adsorption of surfactant (or corrosion inhibitors) molecules on metal surfaces is governed by this strong affinity between polar groups and metal surfaces[7]. To test this hypothesis, we performed molecular simulations of surfactant molecules on metal surfaces. We used a coarse-grained model of a surfactant molecule, with a polar head group and a hydrophobic tail. The polar head group had a strong affinity for the metal surface. In a series of simulations, we varied the hydrophobic interactions between tails of the surfactant molecules. Interestingly, we observed that when the hydrophobic interactions between tails is small, only a weak, random adsorption is observed. When the hydrophobic interactions are increased, a significant increase in adsorption is seen, leading to formation of a self-assembled monolayer (SAM) (Fig. 1 (a) and (b)). These results indicate that the hydrophobic interactions between surfactant tails are responsible for

the formation of ordered adsorbed films of surfactant molecules at the metal-water interface. We also investigated how the size of the polar head group affects the adsorption morphology. We found that when the polar head group is large, surfactant molecules aggregate and adsorb on surfaces in cylindrical micelles (Fig. 1(c)). This work has been published in the Journal of Chemical Physics B[6].

RESEARCH AIMS

I have three broad research aims: **Aim 1:** To understand the relationship between surfactant chemistry, metal-surface chemistry and concentration on the adsorption behavior. **Aim 2:** Investigate how different adsorption morphologies affect the physical and electrochemical properties of metal surfaces. **Aim 3:** To design optimum corrosion inhibitor molecules. Research design and methodology for achieving each of these aims is discussed in the next section.

METHODOLOGY

To succeed in **aim 1**, I will use the coarse-grained representation of surfactant molecules (described previously) to study how different parameters such as chemistry of the molecules, surface properties and solution conditions affect the adsorption phenomena. In a coarse-grained approach, few atoms in a molecule are lumped together to form a united atom or a bead. Furthermore, explicit solvent molecules are not incorporated in the simulations, but their average effect is included via Langevin dynamics. These simplifications help to significantly enhance the time- and length-scales possible to achieve in a simulation. Even with these simplifications though, I find that the formation of a SAM takes more than 8 weeks of computer time with the simulation running in parallel on 8 processors. To identify the most stable adsorption configuration, I will perform free energy calculations using weighted histogram techniques. In **aim 2**, I plan to use all-atom simulations in which atoms of surfactant molecules as well as solvent and counter-ions are explicitly incorporated in the simulations. Based on the adsorption morphologies identified in aim 1, I will design these morphologies in all-atom representation. After equilibrating the simulation system, I will calculate ion diffusion, water diffusion and hydrophobicity of metal-water interface using Indirect Umbrella Sampling (INDUS) calculations[8]. In **aim 3**, results from aim 1 and aim 2 will be evaluated to identify and design the best surfactant molecules for achieving maximal and robust corrosion inhibition. I expect that the most optimum surfactant design will depend on surface chemistry and solution conditions (concentration, ionic strength, etc.).

ANTICIPATED OUTCOMES

I expect that with my research, we will have a fundamental understanding of the relationship between surfactant and metal chemistry, adsorption behavior and corrosion inhibition. This knowledge will help design new robust corrosion inhibitor molecules for testing in experimental labs as well as in field conditions.

PRIMARY GOALS DURING THE YEAR OF FUNDING

I will plan to complete aim 1 (coarse-grained simulations) during the year of funding. Based on the results of aim 1, I will also start generating all-atom molecular simulation systems. I plan to learn how to perform free energy calculations in molecular simulations using techniques such as umbrella sampling and weighted histogram methods during this year. Furthermore, I have also started learning density functional theory (DFT) calculations which will be useful for performing quantum-level simulations, if required.

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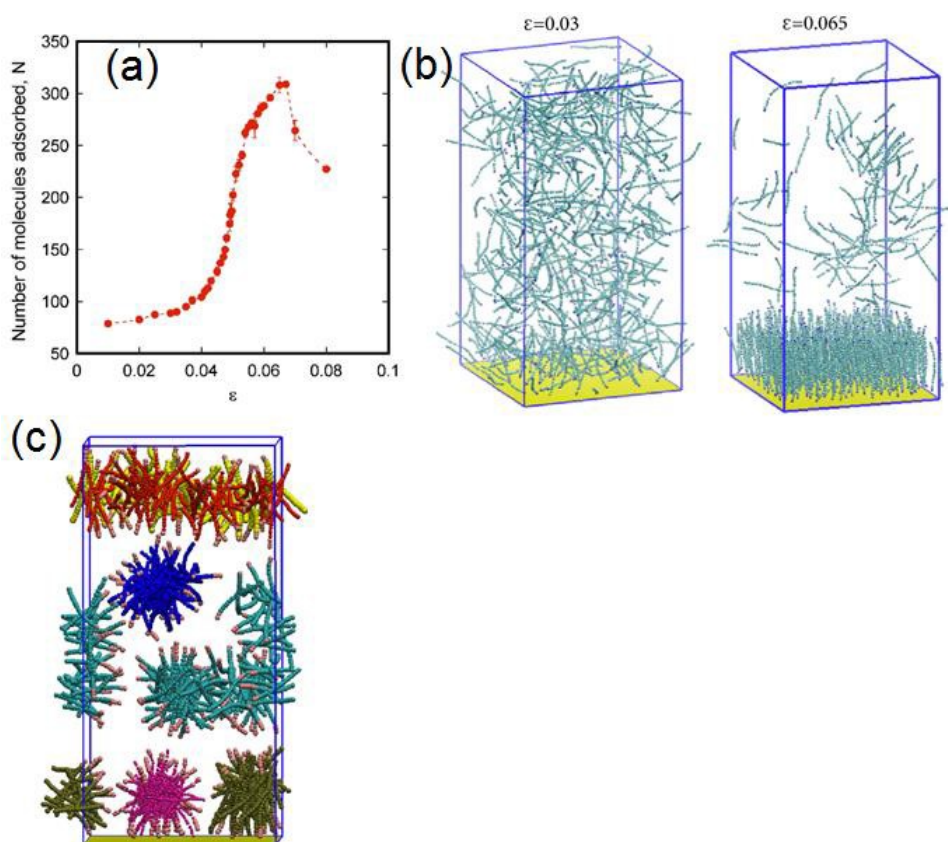
Fig 1. (a) Number of surfactant molecules adsorbed on the metal surface as a function of the strength of hydrophobic interactions between the surfactant tails, ε. Significant increase in adsorption is observed when the ε increases. (b) Snapshots of simulation system. For ε = 0.03, random adsorption is observed. For ε = 0.065, a self-assembled monolayer is observed. (c) Cylindrical micelles in the adsorbed and aggregated phase observed when the polar head group is larger than the surfactant tails.