

PRF# 56892-DNI6

Project title: Molecular mechanisms of corrosion inhibitors studied using molecular simulations

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Overview. Corrosion inhibitors are surfactant molecules that are injected in oil-and-gas pipelines to inhibit internal corrosion. It is understood that these molecules adsorb onto metal surfaces to form self-assembled layers. There are significant gaps in our understanding of the mechanism(s) by which these molecules retard corrosion upon adsorption. In this research, we are performing molecular simulations to understand the factors that affect the adsorption behavior of these molecules on metal surfaces. We have taken two different directions:

1. Understand the adsorption and self-assembly of inhibitor molecules using coarse-grained models.
2. Study adsorption and aggregation of inhibitor molecules in fully-atomistic models.

Coarse-grained simulations. A corrosion inhibitor molecule is modeled as a bead-spring, semi-flexible, linear molecule. The first bead represents the polar head group and the remaining beads represent the alkyl tail. Metal surface is modeled as a smooth surface which has a strong affinity for the polar head bead. The tail beads have attractive interaction for each other representative of the hydrophobic effect. Solvent molecules are not included explicitly in the simulation system. We have studied adsorption behavior of a finite concentration of inhibitor molecules near a metal surface by performing Langevin dynamics simulations. The following are the *key findings* from this work:

1. Hydrophobic interactions between alkyl tails play an important role in the formation of adsorbed self-assembled layers¹. We perform a series of simulations wherein we change the strength of hydrophobic interactions between the tails while keeping the interaction between the polar head and the metal surface to be the same. Fig. 1 shows that when the interaction between the tails, ϵ is weak, only a small amount of adsorption is observed. As the strength of hydrophobic interactions is increased, a significant increase in the adsorption occurs leading to the formation of a self-assembled monolayer (SAM). It is concluded that a strong interaction between the polar-head of inhibitor molecules and the surface is not sufficient for formation of an adsorbed SAM.

Importance: The general presumption in the corrosion community has been that a strong affinity of the polar-head group for the metal surface is solely responsible for the adsorption of inhibitor molecules. Alkyl tails only facilitate corrosion inhibition via forming a hydrophobic barrier to retard the approach of water and corrosive species. This work shows that alkyl tails also play an important role in the adsorption process.

2. Morphology of the adsorbed layer is governed by the geometry of the molecule¹. In these simulations, we investigate how the adsorption behavior changes when the size of the polar bead is twice the size of the hydrophobic bead. We find that for this molecular geometry, the molecules adsorb as cylindrical micelles on the metal surface (Fig. 2).

Importance: Often, inhibitor molecules with large and bulky polar groups are tested with the assumption that a strongly polar head group will result in better corrosion inhibition. However, little importance is given to the molecular geometry. An adsorbed layer with cylindrical micelles may have significantly different corrosion inhibition properties.

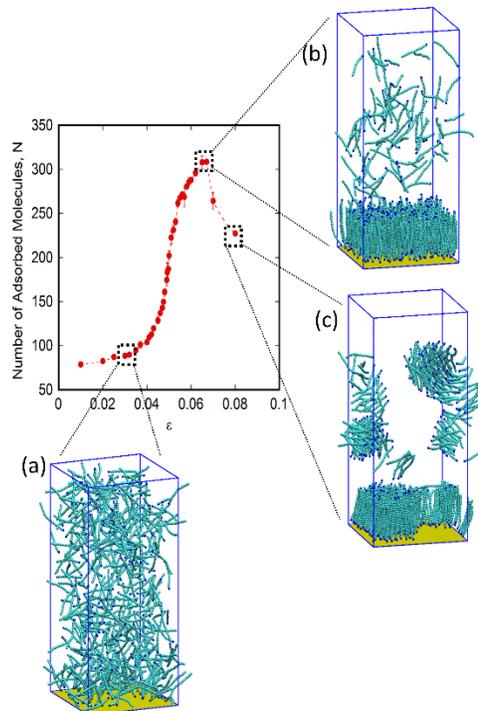


Fig. 1. Number of inhibitor molecules adsorbed on surface as a function of strength of interaction between the tails, ϵ . Snapshots of adsorbed configuration are shown for (a) $\epsilon = 0.03$ (random adsorption), (b) $\epsilon = 0.065$ (SAM), and (c) $\epsilon = 0.07$ (aggregates of molecules in bulk and on surface)

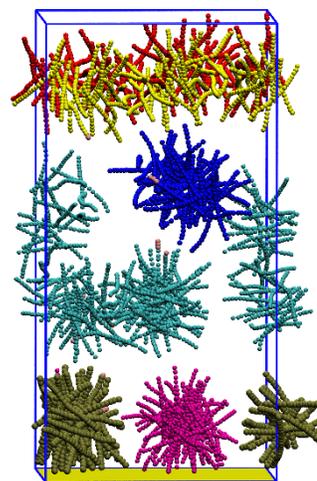


Fig. 2. Cylindrical micelles of inhibitor molecules in the bulk and the adsorbed phase.

Atomistic Molecular Dynamics (MD) Simulations. In this work, we have performed atomistic MD simulations of corrosion inhibitor molecules near a metal-water interface. Four different molecules have been studied: imidazolium-based surfactants of 10-carbon (Imid-10) and 17 carbon (Imid-17) tail length as well as quaternary-ammonium surfactants of 10-carbon (Quat-10) and 16-carbon (Quat-16) tail length (Fig. 3). These molecules aggregate in the bulk phase to form spherical micelles. Following are the *key findings* from this work²:

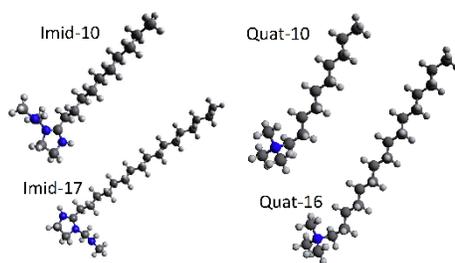


Fig. 3. Different corrosion inhibitor molecules studied.

1. Un-aggregated inhibitor molecules show a strong affinity to adsorb onto metal surface. We employ umbrella sampling to determine the free energy of adsorption of inhibitor molecules on metal surface in infinite dilution. We find that the inhibitor molecules strongly adsorb on the metal surface with a free energy of adsorption of $\sim 30 k_B T$. The free energy of adsorption is found to be independent of the tail-length of the molecules.

2. Inhibitor micelles show a weak tendency to adsorb and experience a long-range repulsion from the metal surface. For the inhibitor micelles formed in bulk, we calculate their free energy of adsorption on the metal surface using umbrella sampling. The micelles comprise of 18 to 19 molecules and have a radius of $\sim 15 \text{ \AA}$. These micelles experience a repulsion even at distances of 50-60 \AA from the surface (Fig. 4). We find that the long-range repulsion is a result of the interaction between the corona of the counter-ions and the solvation shell of the micelle with the adsorbed layers of water on the metal surface.

Importance: A long-standing question in the oil-and-gas industry has been to determine the optimum concentration of corrosion inhibitor molecules to be injected for best performance. Our results indicate that higher concentration is not always better. This is so because above the critical micelle concentration, the inhibitor molecules form micelles which have a weak tendency to adsorb.

3. Kinetics of SAM formation involves many distinct steps. The adsorption kinetics occur in three steps: first step involves rapid adsorption. In this step, molecules adsorb with their polar groups towards the surface. The second step is slower. In this step, the distinct islands of adsorbed molecules merge to form a contiguous layer. In the third step, molecules adsorb only in the configuration in which their polar groups point towards the solution. Therefore, the SAM is like a partial bilayer of adsorbed molecules.

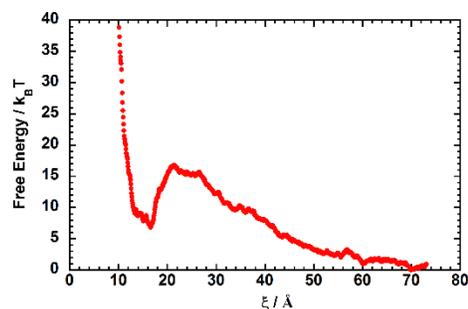


Fig. 4. Free energy profile of Imid-17 molecule as a function of distance from the metal surface, ζ

Impact of ACS PRF grant on PI's career

This grant has been extremely important for PI's research. The PI was able to support four graduate students from this grant, which would not have been possible. This research is different from what the PI did during graduate studies and post-doctoral appointment. This grant therefore allowed the PI to venture into a new field. The preliminary results from this grant helped the PI secure experimental collaborations within the university and helped him in getting an NSF grant in a collaborative project. The PI believes that ACS PRF grants have been extensively helpful to new faculty members in the US universities. They help new investigators to ramp up their research so that they can compete for larger grants.

Impact of ACS PRF grant on students

This grant has helped provide stipend to two masters and two PhD students. The stipends have helped the students to focus solely on research and make good progress in their studies. They have got the opportunity to present their research at various national and international conferences and publish journal articles. A masters student (Mohsen Ghasemi) successfully completed the program and have joined a top-ranking university as a PhD student.

REFERENCES

1. Ko, X.; Sharma, S., Adsorption and Self-Assembly of Surfactants on Metal–Water Interfaces. *J. Phys. Chem. B* **2017**, *121* (45), 10364-10370.
2. Kurapati, Y.; Sharma, S., Adsorption Free Energies of Imidazolium-type Surfactants in Infinite Dilution and in Micellar State on Gold Surface. *J. Phys. Chem. B* **2018**, *122*, 5933-5939.