

Aggregation and Adsorption Behavior of Organic Corrosion Inhibitors studied using Molecular Simulations

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ABSTRACT

We have performed all-atom classical molecular dynamics simulations of aggregation and adsorption of different corrosion inhibitor molecules on metal surfaces. We report free energies of aggregation and adsorption of imidazolinium-type (henceforth referred to as imid) and quaternary ammonium-type (referred to as quat) corrosion inhibitors of different alkyl tail lengths. Corrosion inhibitor molecules show a strong tendency to adsorb onto metal surfaces in the unaggregated state. Inhibitor micelles, on the other hand, experience a free energy barrier to adsorption. The quat micelles are found to be thermodynamically stable in the adsorbed state whereas the imid micelles are only metastable in the adsorbed state. Quat micelles deform and partially disintegrate upon adsorption, which renders stability, while the imid micelles do not deform. The inhibitor molecules demonstrate a strong tendency to aggregate into micelles in the aqueous phase. The micellization free energy is found to be $\sim 68 k_B T$ for a micelle comprising of 18 molecules of imid molecules.

Key words: corrosion inhibitors, aggregation, adsorption, free energy

INTRODUCTION

Corrosion of transportation pipelines is a major concern for the oil and gas industry. Majority of oil and gas transportation pipelines are made of low alloy carbon steel. They are prone to internal corrosion because of the presence of water in oil and gas stream.

The use of corrosion inhibitors is an effective way of retarding internal corrosion of low alloy carbon steel pipelines.¹⁻³ Corrosion inhibitors are the surface-active chemical compounds which when injected into an oil pipeline in small concentrations, reduce corrosion by preferentially adsorbing onto the metal surface. However, there is a search for more robust corrosion inhibitors which can work in varying solution conditions and are environmentally friendly.⁴⁻⁷ Furthermore, even though corrosion inhibitors are widely used in the oil-and-gas industry, the actual mechanism of action is not yet understood.⁸ As a result,

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search of new molecules which act as good corrosion inhibitors has largely been based on trial and error experimentation. This has hindered the progress of finding more effective inhibitors.

It has been suggested via many experimental studies that corrosion inhibitor molecules adsorb in organized layers on metal surfaces. However, the adsorption and self-assembly of inhibitor molecules on metal surfaces has not been systematically investigated at the molecular level.⁹⁻¹⁵ The solution environment is complex with a large number of species present and the difficulty of probing nanometer-sized length scales at the metal-water interface makes the problem difficult to study in experiments.¹⁶ There have been inconsistencies between the adsorption morphologies predicted from different experimental methods. Methods like electrochemical quartz crystal microbalance (EQCM), saturation adsorption data, electrochemical impedance spectroscopy (EIS), laser scattering have predicted that the inhibitors adsorb in planar, self-assembled layers, on the other hand, atomic force microscopy (AFM) experiments have revealed that inhibitors adsorb in various morphologies such as self-assembled monolayers (SAMs), spherical or cylindrical micelles, or hemimicelles.¹⁷

In this work, we have employed classical molecular dynamics simulations to study the behavior of imidazolinium-based and quaternary ammonium-based molecules, which are among the widely used corrosion inhibitors in the oil-and-gas industry,^{8, 16, 18-21}. Inhibitor molecules can exist in several phases near the metal-water interface such as the un-aggregated phase, micellar phase and adsorbed phase. The overall goal of our research is to determine the relative stability of each phase and the nature of transitions between them. This work is follow-up of the work performed by Kurapati and Sharma.¹⁷

SIMULATION METHODOLOGY

Simulation Models. The simulation system comprise of inhibitor molecules in an aqueous solution. We have studied four different corrosion inhibitor molecules: two imidazolinium-type molecules with 10 and 17 carbon long tails (referred to as Imid-10 and Imid-17 respectively), and two quaternary ammonium-type molecules with 10 and 16 carbon long tails (referred to as Quat-10 and Quat-16 respectively). The structures of these imid and quat molecules are shown in Figure 1.

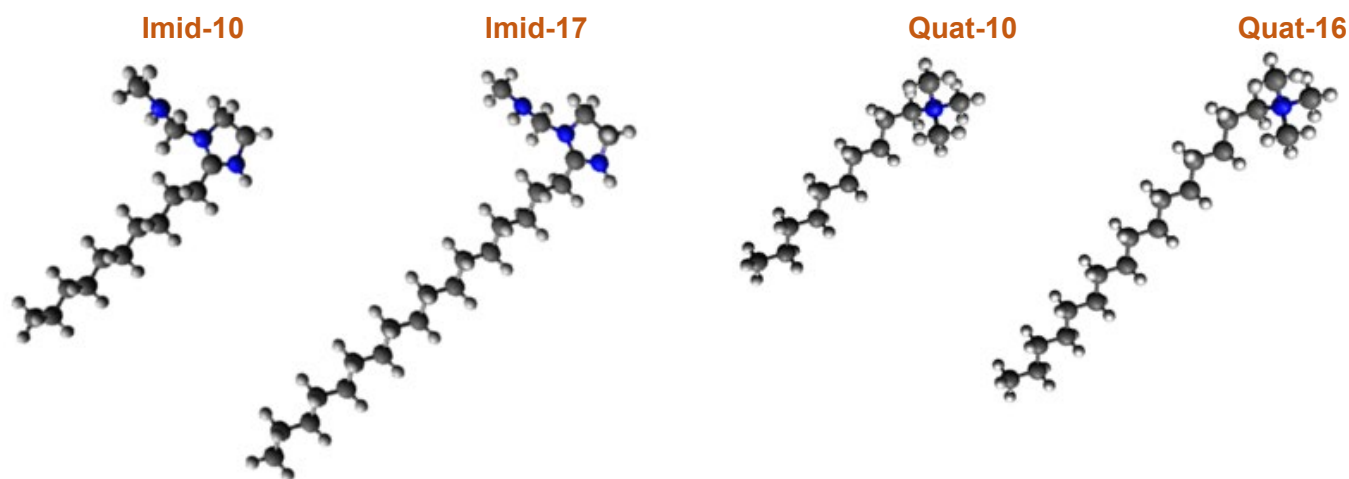


Figure 1: Structure of the imid and quat molecules employed in this study. Blue beads represent nitrogen atom, dark gray beads represent carbon atoms and light gray beads represent hydrogen atoms.

Partial charge on each atom of the inhibitor molecules is determined in the presence of implicit water (as solvent) using Density Functional Theory (DFT) with GAUSSIAN-09 software. DFT level theory of B3LYP and 6-31G (d,p) orbital basis sets are used. Classical interaction potential parameters of inhibitor molecules are obtained from General Amber Force Field (GAFF), which is a widely used force field for

organic molecules.²² Water is represented by SPC/E (simple point charge enhanced) water model.²³ The head group of the inhibitor molecules are protonated with an overall charge of +1 and therefore one chloride ion per inhibitor is introduced in order to keep the entire system charge-neutral. The interaction parameters for chlorides is taken from Joung-Cheatham model,²⁴ which is a widely used force field for alkali and halide ions in explicit water.

Metal surface is represented by six layers of gold atoms arranged in a close-packed face-centered cubic (fcc) lattice plane (111) with the lattice constant of 4.08 Å. Gold metal is chosen because its interaction potential parameters are available from the Interface force field.²⁵

Simulation System Setup. For simulations of inhibitor molecules in aqueous medium in the absence of any metal surface, the simulation box is taken periodic in all three dimensions X, Y and Z. The size of the simulation box is chosen as 50 Å X 50 Å X 50 Å for inhibitor in infinite dilution and 65 Å X 65 Å X 65 Å for the micelles. The bigger box size is taken to avoid interaction of micelles with their periodic images. The system with a metal surface is represented by a simulation box which is periodic only in the X and Y dimensions. The Z dimension of the simulation box is bound by metal surface on one end and a non-interacting reflecting surface on the other end. The size of the aqueous column above the gold lattice is chosen as 50 Å X 50 Å X 50 Å for inhibitor in infinite dilution and 65 Å X 65 Å X 150 Å for the micelles. A considerably long water column of 150 Å is considered for the micelles because our simulations revealed that they exhibit long-ranged interactions with the metal surface.

All the MD simulations were performed using Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD simulations package.²⁶

RESULTS

Behavior of Inhibitors in Bulk Aqueous Phase

In the bulk aqueous medium, both imid and quat molecules are found to aggregate in the form of spherical micelles. Snapshots of some micelles are shown in Figure 2. It can be seen that the inhibitors aggregate in such a way that the polar head groups remain exposed to water while the hydrophobic alkyl tails occupy the interior of micelle. This kind of arrangement of molecules is observed because the hydrophobic tails prefer to hide away from water molecules.

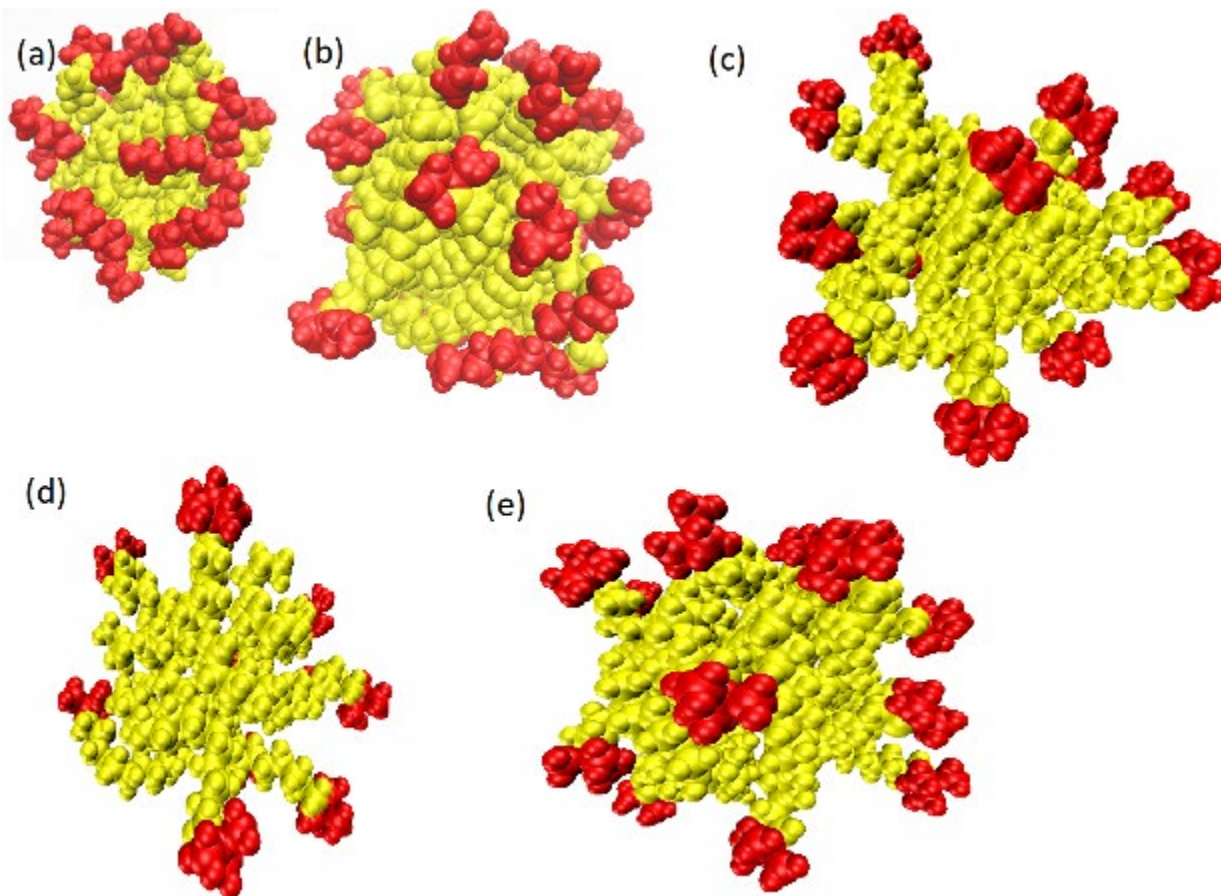


Figure 2: Snapshots of (a) an Imid-10 micelle comprised of 18 molecules, (b) an Imid-17 micelle comprised of 19 molecules, (c) a Quat-10 micelle comprised of 18 molecules, (d) and (e) Quat-16 micelles comprised of 10 and 19 molecules respectively. Red beads represent the polar head groups and yellow beads represent the alkyl tails. [Adapted with permission from S. Sharma, et al., "Adsorption Behavior of Organic Corrosion Inhibitors on Metal Surfaces-Some New Insights from Molecular Simulations," CORROSION (2018).]

In order to estimate the shape of these micelles, micelles with different number of molecules (N_{micelle}) are considered in the simulations. The asphericity of the micelles is calculated by the following equation.²⁷

$$\text{Asphericity} = \frac{\lambda_1 - 0.5(\lambda_2 + \lambda_3)}{R_g^2} \quad (1)$$

where λ_i are principle components of the radius of gyration squared tensor. Here, $\lambda_1 > \lambda_2 > \lambda_3$ and R_g^2 is the mean squared radius of gyration. An aphericity value of 0 indicates a perfect sphere.

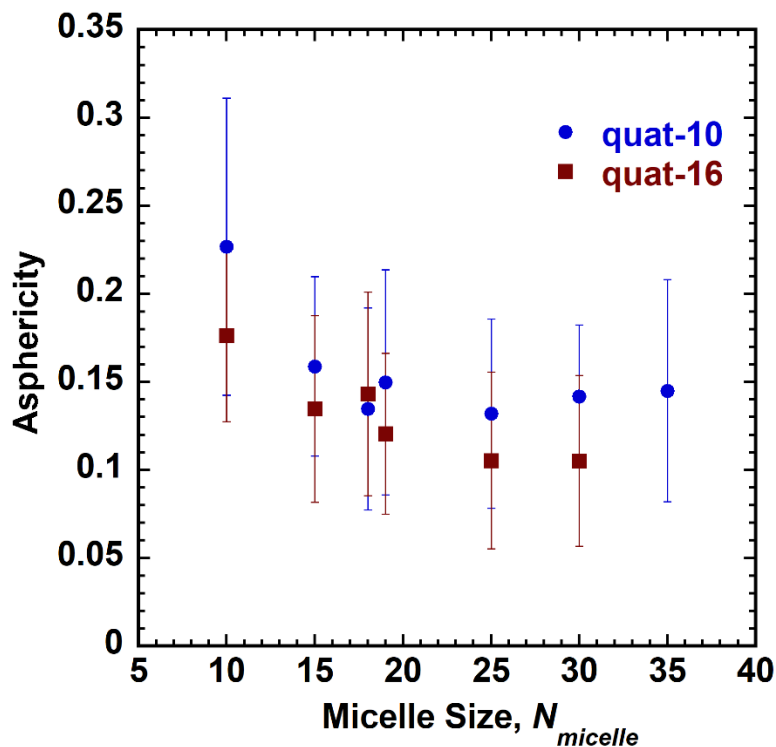


Figure 3: Asphericity of quat micelles as a function of their size, $N_{micelle}$. $N_{micelle}$ is the number of molecules in the micelle.

The asphericity of quat micelles is shown in Figure 3. It is seen that the asphericity values are small and therefore the micelles are spherical in shape, a behavior which was also observed for imid micelles.¹⁷ It is also seen that as the size increases, the micelles become more spherical in shape.

Micellization of Imid Molecules

Aggregation of inhibitors is seen in both imid and quat micelles. We have calculated the free energy of micellization of an imid-10 micelle comprised of 18 molecules. To perform this calculation, we employed free energy perturbation method. In this method, the van der Waals interaction potential acting between imid molecules (V^{intra}) is varied by a perturbation parameter (λ) without varying the interaction between the water molecules. $V^{intra}_{perturbed}$ is shown in the following equation.

$$V^{intra}_{perturbed}(r) = \lambda \cdot V^{intra}(r) \quad (2)$$

When $\lambda=1$, the intra-molecular interaction potential is unperturbed and therefore all the inhibitors aggregate to form a single micelle. However, when λ is sufficiently low (~ 0.65), the intermolecular interaction potential becomes sufficiently weak that the micelle breaks apart (shown in Figure 4).

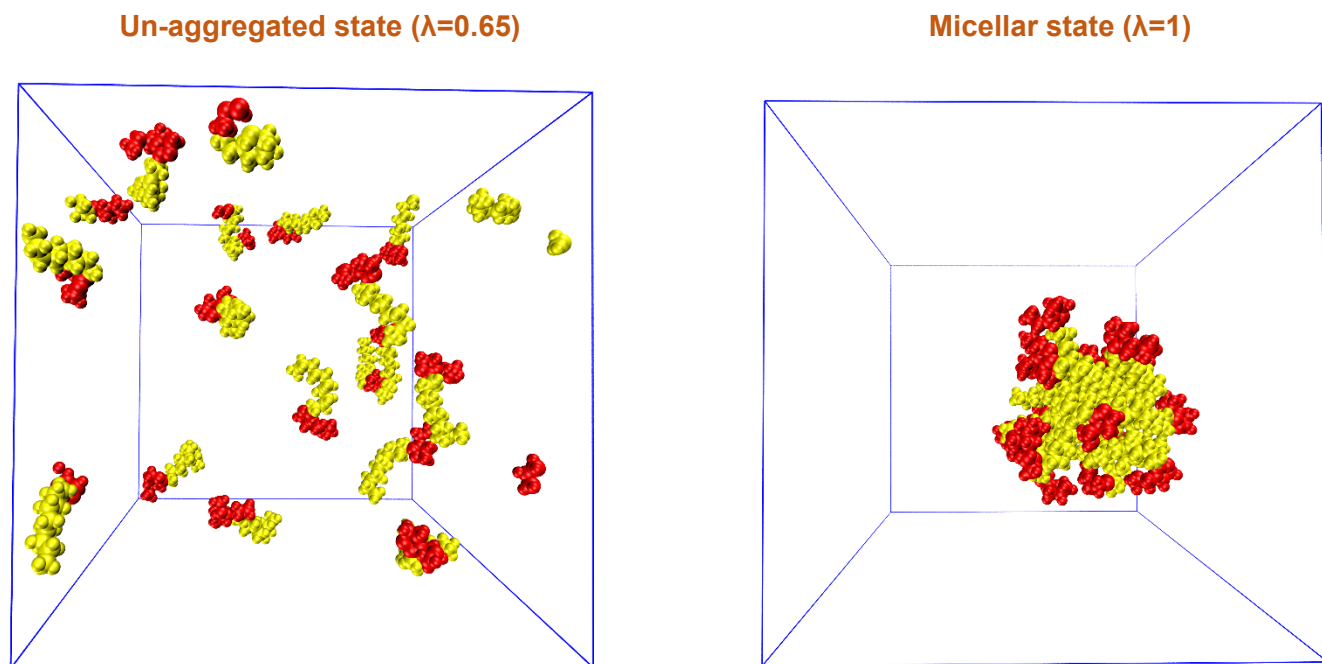


Figure 4: Simulation snapshot showing un-aggregated state ($\lambda=0.65$) and aggregated state ($\lambda=1$). Water molecules and chlorides are not shown for clarity.

By performing a series of simulations in which λ is varied from 0.65 to 1 systematically, a thermodynamic path connecting the un-aggregated state to the aggregated state is generated. Free energy differences are calculated for each increment in λ by using the perturbation theory.²⁸ Upon summing up all the free energy differences corresponding to the λ s, the overall free energy of micellization is determined. This method of obtaining free energy is known as *Thermodynamic Integration*.²⁹

The overall free energy of micellization for this imid-10 micelle is found to be 68.1 ± 2.1 K_BT. This large value of free energy confirms that micellization of imid inhibitors is strongly favored.

Behavior of Inhibitors near Metal-Water Interface

After studying the aggregation of inhibitor molecules, a lattice of gold atoms was introduced as the metal surface in an attempt to understand the adsorption behavior of the molecules. A total of 64 number of imid-17 molecules were injected into the aqueous medium near the metal surface. A snapshot of the equilibrium state of the system is shown in Figure 5. It is observed that most of the molecules aggregated and formed micelles in the bulk aqueous phase while a few unaggregated molecules (4-5 out of 64) adsorbed flat onto the metal surface. The micelles remained in the bulk and did not adsorb onto the surface.

The spontaneous aggregation in the bulk phase can be understood from the largely favorable free energy of micellization as discussed in the previous section. Moreover, the unaggregated inhibitors showed a strong adsorption tendency as opposed to the micelles. In order to understand this behavior, free energies were calculated for adsorption of unaggregated inhibitors and inhibitor micelles.

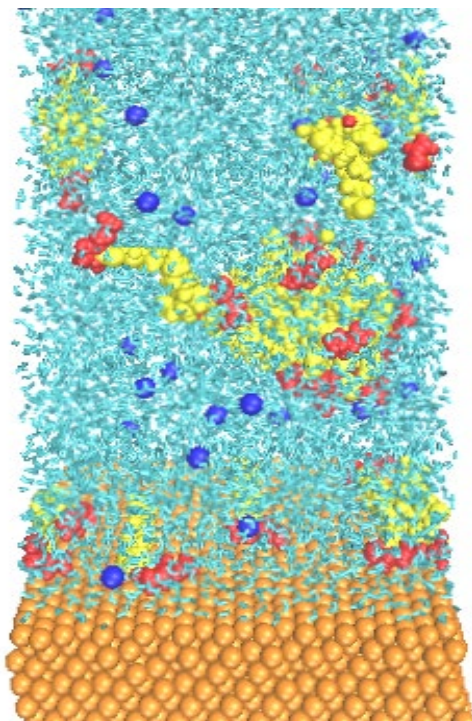


Figure 5: An equilibrated snapshot of the simulation system with 64 Imid-17 molecules in water near a gold lattice. Red beads represent the polar head groups, yellow beads represent the alkyl tails, blue beads represent chlorides. Water molecules are shown in cyan color and the gold lattice is represented by orange color. [Adapted with permission from Y. Kurapati, S. Sharma, "Adsorption Free Energies of Imidazolinium-type Surfactants in Infinite Dilution and in Micellar State on Gold Surface," *The Journal of Physical Chemistry B* (2018).]

Adsorption of Inhibitor Molecules in Infinite Dilution

Simulations were performed to calculate free energy profiles for adsorption of molecules in infinite dilution. This profile is generated by a simulation methodology called Umbrella Sampling.³⁰ In order to generate a free energy profile along a reaction coordinate, the system needs to be sampled well for all relevant values of the coordinate. However, in a conventional molecular dynamics simulation the entire coordinate space is generally not sampled well. In Umbrella Sampling, a biased potential is applied to the system which enables sampling of the entire coordinate space efficiently. In our system, a harmonic biased potential based on the distance of the molecule from the metal surface is applied to the inhibitor molecule. A detailed description of this methodology for a similar system can be found in our research group's previous work.³¹

The free energy profiles for adsorption as a function of distance from the metal surface are shown in Figure 6. It is noted that both the imid and quat molecules adsorb strongly onto the metal surface (with favorable free energies of ~ 32 - 38 $K_B T$) without any considerable free energy barrier. This spontaneous adsorption behavior was also evident in our unbiased MD simulation. Upon adsorption, these molecules lie flat onto the metal surface. The free energy profiles are not smooth because sampling in the orientational space of the molecule is not exhaustive.

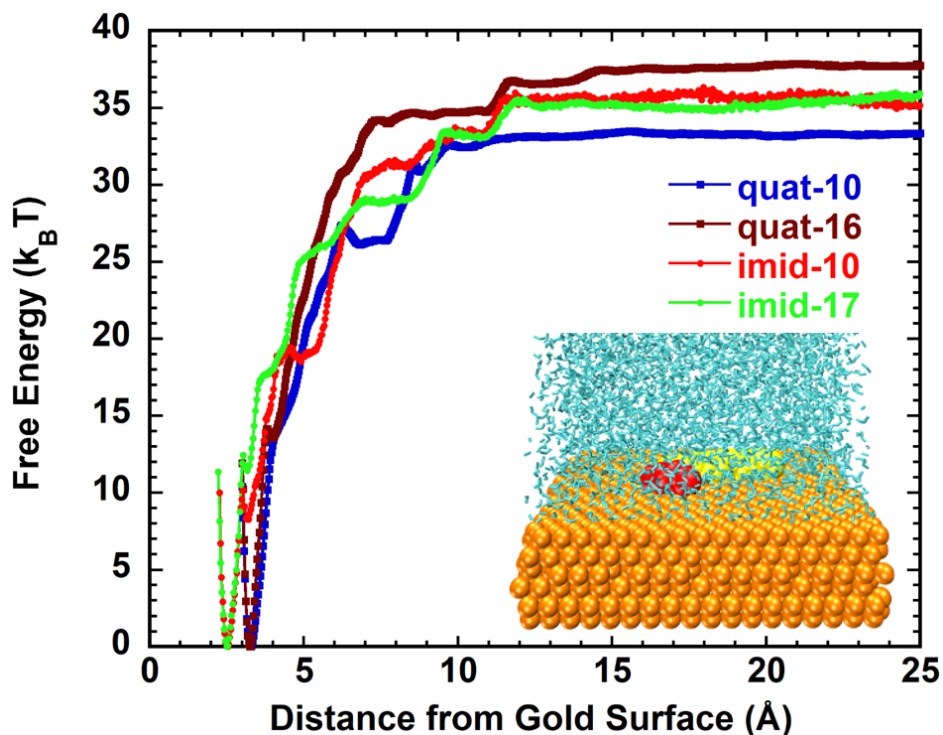


Figure 6: Free energy landscapes for adsorption of inhibitor molecules on gold surface; inset: equilibrium adsorbed configuration of an Imid-17 molecule.

Adsorption of Inhibitor Micelles

By employing a similar Umbrella Sampling methodology, adsorption of micelles is explored with imid and quat micelles. The imid-10 and quat-10 micelles are comprised of 18 molecules and the imid-17 and quat-16 micelles are comprised of 19 molecules (refer Figure 2).

Figure 7 illustrates the free energy profiles for adsorption of the micelles. The landscapes show a large barrier to adsorption of imid micelles (~ 13 $k_B T$ for imid-10, ~ 16 $k_B T$ for imid-17) and also that these micelles experience a long-range repulsion of the order of ~ 50 - 60 Å from the metal surface. This repulsion is attributed to the presence of a large 'corona' of counter-ions and their solvation shell that interacts with the metal surface.¹⁷ However on the other hand, the quat micelles experience a smaller barrier to adsorption (~ 6 - 8 $k_B T$) and are thermodynamically stable in the adsorbed state. The reason for this difference in stabilities of imid and quat micelles is attributed to their behavior near the metal surface.

Figure 8 depicts snapshots of the imid and quat micelles in their adsorbed states. It can be seen that the imid micelle does not deform and stays intact at the metal surface. Quat micelles, on the other hand, are found in the deformed state at the metal surface. This deformation confirms that the adsorbed state of quat micelles is stable.

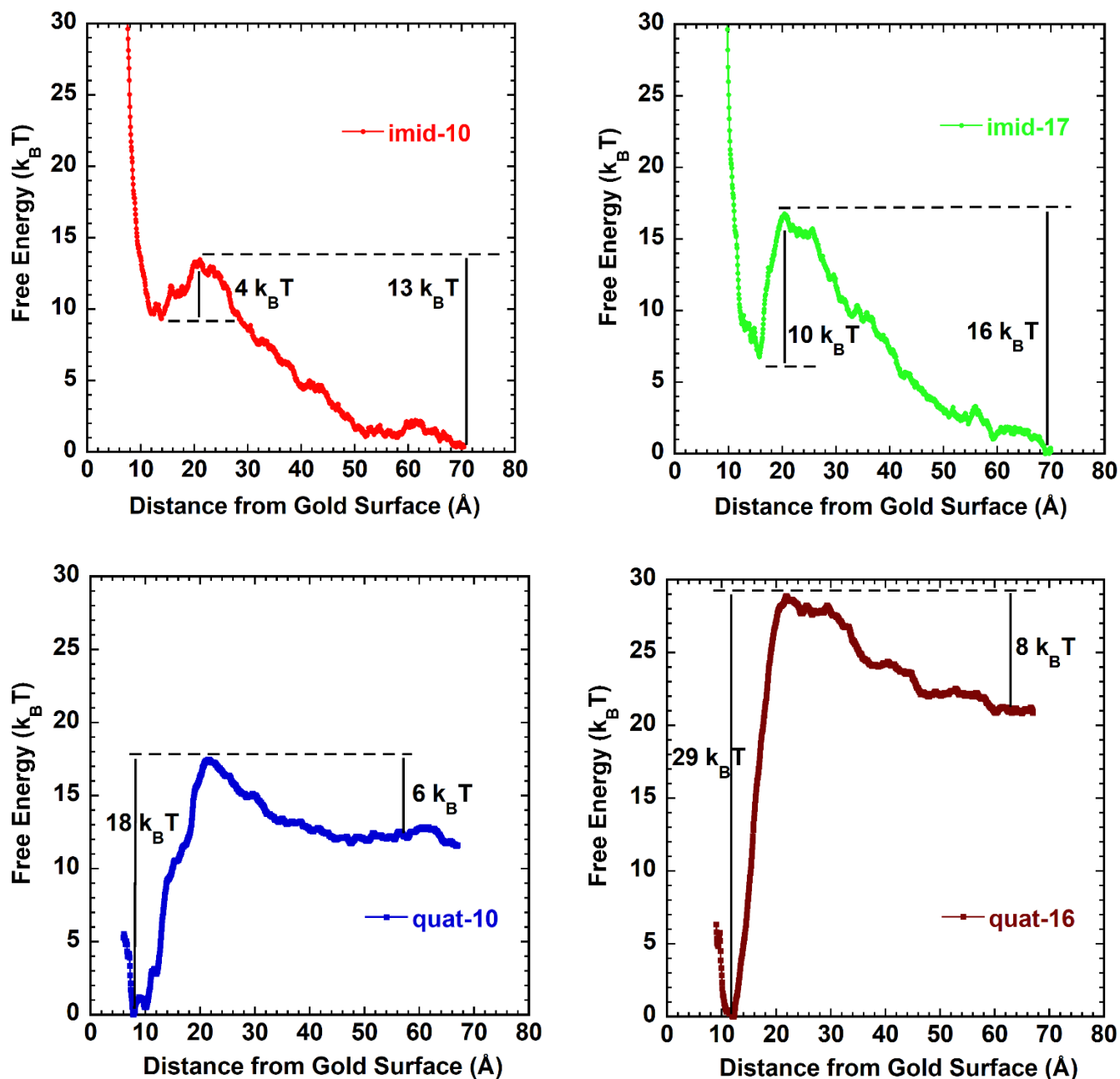


Figure 7: Free energy landscapes for adsorption of inhibitor micelles on gold surface.

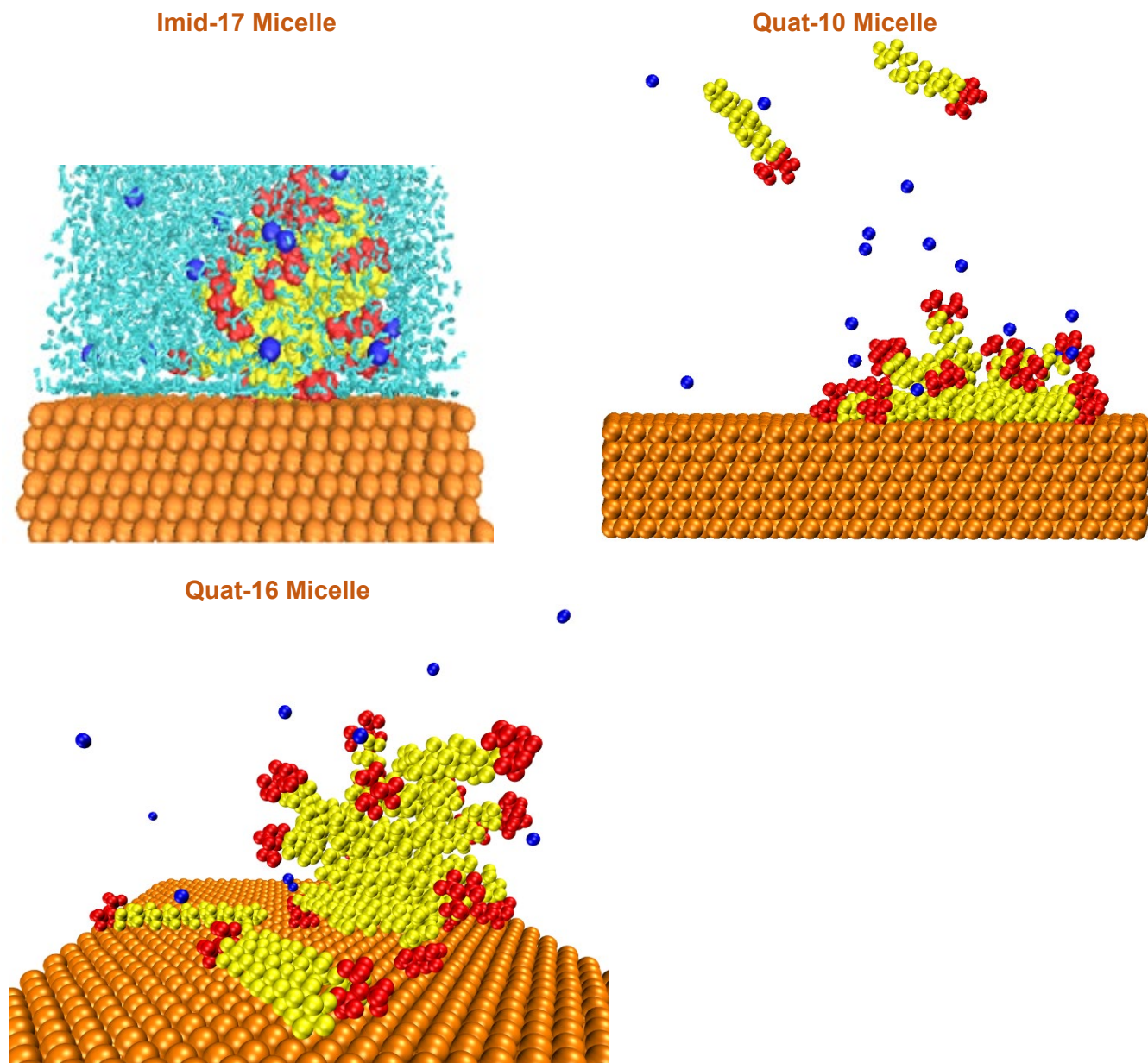


Figure 8: Snapshots of imid and quat micelles in the adsorbed state. Imid micelle remains intact whereas the quat micelles are deformed at the metal surface. Water is not shown in case of quat micelles for clarity. Discrete molecules can be seen that got separated from the quat micelles as a result of deformation.

As opposed to the adsorption of inhibitors in infinite dilution, the adsorption free energy of micelles is obstructed by a free energy barrier. Therefore for better corrosion inhibition, micellization of inhibitors in bulk is unfavorable.

CONCLUSIONS

Corrosion inhibitor molecules can exist in different phases near metal-water interfaces depending upon the stability of their phases. In order to determine the thermodynamic stability, we performed free energy calculations for each phase. The results show that the unaggregated molecules have a strong tendency to adsorb onto the metal surface without experiencing any remarkable free energy barrier. On the

contrary, the inhibitor micelles experience a free energy barrier to adsorption due to the interaction of their counter-ions and solvation shell with the adsorbed water layers on the metal surface. In the bulk aqueous phase, free energy of micellization revealed that micellization is highly favored. This is in consistence with why we see spontaneous aggregation in the bulk aqueous phase rather than surface coverage.

ACKNOWLEDGEMENTS

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