Understanding the Behavior of Surfactant Molecules Near Metal-Water and Air-Water

Interfaces via Molecular Simulations

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This dissertation titled

Understanding the Behavior of Surfactant Molecules Near Metal-Water and Air-Water

Interfaces via Molecular Simulations

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Abstract

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Understanding the Behavior of Surfactant Molecules Near Metal-Water and Air-Water

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In this work, advanced molecular dynamics simulations were employed to study the adsorption of surfactants at metal-water interfaces. A new sampling methodology was developed in molecular simulations that allows efficient sampling of the most thermodynamically stable adsorbed morphology of adsorbed surfactants. The hydration free energies of surfactants and their micelles were also studied. The major findings of this work are: (a) Both unaggregated surfactants and their micelles strongly adsorb on the bare metal-water interfaces; (b) cationic surfactant micelles experience a free energy barrier to adsorption and adsorb by disintegrating on the surface; (c) hydrophobic interactions between the alkyl tails of surfactants promote adsorption, while the accumulation of charged surfactants on the surface inhibits adsorption. As a result, small alkyl tail (C4) quaternary ammonium surfactants adsorb as a sparse layer. Quaternary ammonium surfactants with longer alkyl tails (C12) adsorb as a hemispherical micelle sitting atop a monolayer of adsorbed molecules lying parallel to the surface. Charge neutral surfactants with long alkyl tails, like decanethiol, adsorb in a high-density morphology with molecules standing up on the surface, and a second layer of molecules lying parallel to the surface. (d) Hydration free energy of alkanes is dictated by the entropic loss of water molecules surrounding the alkanes; (e) addition of a hydroxyl

group to the terminal position of the hydrophobic tails of the cationic surfactant molecules helps in reducing their micellization tendency and enhancing their aqueous solubility by two orders of magnitude. Dedication

This dissertation is dedicated to my parents.

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Glossary

- Athermal Surface: A surface which does not have any interaction with any particles in a simulation system. An athermal surface is an impenetrable, hard surface useful for imparting non-periodicity in the simulation system.
- Barostat: In order for a physical system to be at a constant pressure, it needs to be in mechanical equilibrium with the surroundings. Barostats in molecular simulations are methods that simulate this pressure coupling thereby allowing a simulation system to remain at a constant pressure.
- Boltzmann Distribution: The Boltzmann distribution defines the probability with which a system will be in a state, *i* with an energy, E_i and temperature, *T*. The probability of the system to exist in the *i*th state is given by $P_i \propto e^{-\frac{E_i}{k_B T}}$.
- Ensemble: A collection of molecular states or configurations of a system. Some common ensembles are microcanonical ensemble (fixed number of particles N, volume V, and energy E), canonical ensemble (fixed N, V, T) and isobaric-isothermal ensemble (fixed N, P, T).
- Force Field: The interaction potential which governs the motion of the atoms/molecules in a simulation system.
- Harmonic Potential: A potential in which the energy increases as square of the distance from the equilibrium position. Harmonic potential is given by U_b = ¹/₂k(ξ - ξ_o)², where k is the force constant, ξ is the order parameter with respect to which the harmonic potential is applied, and ξ_o is the equilibrium value of the order parameter.

- Langevin Dynamics: A molecular dynamics approach in which solvent molecules are not explicitly included in the system, but their effect on other molecules is included by mimicking the solvent-solute collisions.
- Microstate: The collection of positions and velocities of all the particles of a system at any instant.
- Molecular Simulations: A computational method for studying the behavior of atoms/molecules from the laws of classical or quantum mechanics.

• Partition Function: A thermodynamic function of state variables, such as volume and temperature, of a system that is used to describe several thermodynamic variables of the system, such as pressure, free energy, etc. The partition function for a canonical ensemble is given by $Q = \sum_{i}^{states} e^{-\frac{E_i}{k_B T}}$, where *i* is the index of a microstate and E_i is the total energy of the system in the *i*th microstate.

- Periodic Boundary Conditions: In molecular dynamics simulations of bulk media, the simulation time scales as N^2 , where N is the number of particles in the bulk media. To minimize this simulation time, periodic boundary conditions (PBCs) are introduced. In PBCs, the simulation box is replicated throughout the space to form an infinite lattice. With a sufficiently large size of the original simulation box, the particles of the simulation box do not interact with their periodic replicas. The properties of the bulk media can therefore be studied only by simulating the particles of the original simulation box.
- Phase Space: The collection of all the microstates of a system as the system evolves in a macroscopic condition is called phase space.

- Radial Distribution Function: A distribution profile that shows how the density of a particle varies as a function of its distance from a reference particle.
- Statistical Mechanics: A branch of science that combines the probability theory and statistical methods with the laws of classical or quantum mechanics to obtain thermodynamic quantities, such as free energy, temperature, pressure.
- Thermostat: Like barostats, thermostats are used to maintain the temperature of the simulation system.
- Timestep of a Simulation: Timestep is a fixed amount of time by which the simulation advances. In molecular dynamics simulations, a typical time-step is ~1 fs.
- Umbrella Sampling: A method in molecular simulations that is used to obtain free energy landscape of the system with respect to an order parameter. In this method, a biased potential is applied that promotes sampling of the regions of configuration space which are otherwise hindered by free energy barriers.
- Weighted Histogram Analysis Method: A method used to combine biased probability distributions of different umbrella sampling simulations into a single unbiased probability distribution. The global unbiased probability distribution is then used to obtain free energy as A(ξ) = -k_BT ln P(ξ), where A(ξ) is the free energy at ξ, and P(ξ) is the unbiased probability distribution at ξ.

Chapter 1: Introduction

Adsorption of surfactants on surfaces have several applications such as in froth flotation [1], synthesis of anisotropic metal nanoparticles [2], enhanced oil recovery [3], corrosion inhibition [4], and heterogeneous catalysis [5]. In froth flotation, the surfactants are introduced to selectively adsorb onto mineral surfaces and impart hydrophobicity. The hydrophobicity causes the mineral particles to float, which are then skimmed off the cell and separated [1]. In the synthesis of anisotropic metal nanoparticles, surfactants selectively adsorb on certain facets of metal nanoparticles, thereby allowing growth of the nanoparticles along other directions that results in anisotropic shapes such as nanorods, which are useful in applications like bioimaging, and drug delivery [2]. In enhanced oil recovery, surfactants adsorb onto the carbonate surfaces and alter their wettability from oil-wet to water-wet, as a result of which the adsorbed oil molecules on rock surfaces become available for extraction [3]. Corrosion inhibition of oil pipelines is another important application, wherein surfactant molecules are introduced in the process stream in the oil and gas pipelines. These molecules are understood to adsorb on to the metal surface, which acts as a barrier against ingression of water molecules. This helps in reducing internal corrosion of the pipelines [4]. The focus of this research is to understand the adsorption behavior of surfactant molecules, which are widely used for corrosion inhibition of oil pipelines. These surfactants are called corrosion inhibitors.

1.1 Corrosion

Corrosion is deterioration of metal as a result of electrochemical reaction(s) with its surrounding environment. The stability of a metal depends on its oxidation/reduction potential (ORP) and pH of the environment. Iron, for example, is unstable at zero ORP and therefore it corrodes and forms Fe^{2+} or Fe_2O_3 depending on the solution pH and/or availability of oxygen. Corrosion occurs when two electrochemical reactions take place simultaneously at the cathodic and anodic sites (Equations 1.1 and 1.2) [6].

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$
 at cathode (1.1)

$$M \rightarrow M^+ + e^-$$
 at anode (1.2)

Presence of water is the main cause of corrosion. H^+ , O_2 and H_2O are some of the common oxidizing species which are responsible for cathodic reactions. The surface iron atoms lose electrons at anodic sites, which are accepted by the oxidizing species at cathodic sites. The oxidized iron atoms, Fe^{2+} thereupon form an oxide or dissolve in the aqueous medium.

Common ways to mitigate corrosion include use of protective coatings, corrosion resistant alloys, corrosion inhibitors and cathodic/anodic protection. Cathodic and anodic protection involves bringing the ORP of metal out of the corrosion-prone zone. Corrosion resistant alloys lessen corrosion by forming a passive film on the surface which reduces further corrosion. Protective coatings and corrosion inhibitors mitigate corrosion by forming a layer on the metal surface and preventing the ingression of corroding species to the surface. Of all these methods, protective coatings and cathodic protection can only be used to prevent external corrosion of oil pipelines [7]. Internal corrosion, however, could

be controlled by the use of corrosion resistant alloys or corrosion inhibitors [6, 8]. High alloy corrosion resistant alloys are not a viable option on a large scale due to their high capital cost. Corrosion inhibitors, on the other hand, are proven to be the most appropriate method for preventing internal corrosion because of their low cost and ease of implementation.

1.2 Corrosion Inhibitors

Corrosion inhibitors are the molecules which when injected in ppm concentration, retard internal corrosion of metallic surfaces. The inhibitors act by forming a film on the metal surface, which acts as a barrier to water molecules thereby blocking one or more electrochemical reactions to occur at the metal surface. Corrosion inhibitors are broadly classified based on their composition and mechanism.

1.3 Classification of Corrosion Inhibitors

1.3.1 Passivating Inhibitors

Passivating inhibitors function by forming passive films on the metal surface. These can be of two types: oxidizing anions, such as chromates, nitrates which can passivate steel in the absence of oxygen and nonoxidizing ions, such as tungstate and molybdate, which require oxygen to passivate the steel [9].

1.3.2 Precipitation Inhibitors

Precipitation inhibitors are compounds which form precipitates on the metal surface. Silicates and phosphates are some common compounds which form precipitates with the metallic ions (such as FePO₄, Fe₂SiO₄) and retard corrosion [9].

1.3.3 Adsorption Inhibitors

Adsorption-type inhibitors are the surfactant molecules which adsorb onto the metal surface and act as a barrier to the water molecules. Organic surfactant molecules, which possess a polar head group and a hydrophobic alkyl tail, are the common adsorption-type inhibitors which are used in the oil-and-gas industry. When present in enough concentration, these molecules affect both the anodic and cathodic sites by providing a barrier to anodic oxidative dissolution and a barrier to cathodic reduction. A schematic diagram of a typical organic inhibitor molecule is shown in Figure 1.1 (a). About 80% of commercial inhibitors fall into the category of adsorption-type inhibitors, because of their high inhibition efficiency and low cost [9, 10]. Figure 1.1 (b, c) show chemical structures of imidazolinium-type and quaternary ammonium-type corrosion inhibitors, which are some of the widely used inhibitor molecules in the oil-and-gas industry [11-14].



Figure 1.1. (a) Schematic diagram of adsorption-type inhibitor [4]; (b) structure of an imidazolinium-type surfactant molecule; (c) structure of a quaternary ammonium-type surfactant molecule. The subscript n indicates length of the alkyl tail.

Apart from surface-active compounds, environmental conditioners are also used for corrosion inhibition. They aim at removing corrosive reagents from the solution. For example, sodium sulfite and hydrazine are used as oxygen scavengers which remove dissolved oxygen from the aqueous medium, as shown in Equations (1.3) and (1.4) [6]. $2Na_2SO_3+O_2 \rightarrow 2Na_2SO_4$ (1.3)

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2 \tag{1.4}$$

These compounds are, however, effective only where oxygen reduction is the main cathodic reaction. The focus of this work is on adsorption-type organic corrosion inhibitor molecules.

1.4 Measurement of Corrosion Inhibition

Rating of a corrosion inhibitor is done based on a factor called Inhibition Efficiency (IE) (Equation 1.5) [10].

$$\text{IE}(\%) = \frac{CRu - CRi}{CRu} * 100 \tag{1.5}$$

where, CR_u is the corrosion rate without inhibitor and CR_i is the corrosion rate in the presence of inhibitor. Corrosion rate is usually measured by methods such as linear polarization resistance monitoring, adsorption isotherm, measurement of electrical double capacitance at the metal-solution interface [15-17].

1.5 Adsorption Mechanism

Organic inhibitors are the most effective corrosion inhibitors because of their ability to block anodic and cathodic reactions upon adsorption [6]. Adsorption is known to be mainly driven by the affinity of polar head group to the metal surface [18]. The role of alkyl tails is to render a hydrophobic film on the metal surface, which would keep the water molecules away from the surface [19].

Adsorption process can either be classified as *physisorption* or *chemisorption*. The process depends upon the chemistry of polar head group and the metal surface. Physisorption refers to physical adsorption without the formation of a chemical bond between the molecules and the surface atoms [20]. Chemisorption involves chemical bonding between the inhibitor and the metal. However, kinetics of chemisorption are generally slower than physisorption [20].

Inhibition efficiency is expected to be dependent on how effectively a surface is covered by adsorbed inhibitors [21]. However, designing an inhibitor molecule which can provide optimum surface coverage is a difficult task. There are several factors which govern the adsorption process. Even for the simplest of systems, the interactions between the inhibitor polar head groups, hydrophobic alkyl tails, water molecules, and metal surface must be studied methodically. Above a critical concentration, the critical micelle concentration (CMC), inhibitor molecules aggregate to form micelles in the bulk aqueous phase. Formation and adsorption of the inhibitor micelles also needs to be explored.

1.6 Adsorption Morphologies

Surface characterization techniques, such as atomic force microscopy (AFM), quartz-crystal microbalance (QCM), sum-frequency generation microscopy (SFG), and scanning tunneling microscopy (STM) have been useful for predicting the adsorption morphologies of surfactant molecules on polar surfaces such as mica, silica, and gold surfaces [22-24]. Figures 1.2 (a, b) show the AFM images of imidazolinium-type surfactant molecules on mica surface [24]. From the topographic images, it is postulated that at 0.5 CMC, the surfactant molecules adsorb as a monolayer in the standing-up configuration and at 2 CMC concentration, the surfactant molecules adsorb in a bilayer.



Figure 1.2. AFM images of adsorption of imidazolinium-type surfactant molecules on mica surface at (a) 0.5 CMC; and (b) 2 CMC concentration. Reproduced with permission from Xiong, *et al.*, "Atomic force microscopy study of the adsorption of surfactant corrosion inhibitor films." Corrosion 70.3 (2013): 247-260

The AFM images for the quaternary ammonium type surfactant molecules on silica and mica surfaces obtained by Manne, *et al.*, are shown in Figure 1.3 (a) and Figure 1.3 (b) respectively [22]. They find that quaternary ammonium type surfactant molecules

adsorb as spherical aggregates on a silica surface and cylindrical aggregates on a mica surface. Wang, *et al.*, have performed *in situ* tapping mode AFM measurements and have found that the quaternary ammonium surfactants form a porous film consisting of patches of molecules standing-up in a tilted orientation, and dynamic empty spaces on the mica surface, indicating that the surfactant molecules do not fully cover the mica surface (Figure 1.4) [25].



Figure 1.3. AFM images revealing adsorption of quaternary ammonium-type surfactant molecules as (a) spherical aggregates on silica surface at 2 CMC; and (b) cylindrical aggregates on mica surface at 2 CMC. Reproduced with permission from Manne, Srinivas, and Hermann E. Gaub. "Molecular organization of surfactants at solid-liquid interfaces." Science 270.5241 (1995): 1480-1482



Figure 1.4. In-situ tapping mode AMF image of quaternary ammonium-type surfactant molecules revealing a porous adsorption morphology on mica surface. The black spots indicate empty spaces on the mica surface. Reproduced with permission from Wang, *et al.*, "Investigation of Inhibitor Adsorption Mechanism by in Situ Tapping Mode Atomic Force Microscopy." AMPP Corrosion/2021, #16610.

Jascke, *et al.*, have performed contact mode AFM measurements for adsorption on gold surfaces and reported that the bromide counter-ions play a crucial role in determining the adsorption morphology of surfactant molecules [26]. They found that bromides adsorb preferentially to the gold surface and stabilize the cationic head groups of surfactant molecules leading to the formation of full cylindrical micelles. The adsorption of cetyltrimethylammonium hydroxide (C_{16} TAOH) molecules, is however, dominated by the lateral interactions between their alkyl tails and the gold surface, leading to the formation of hemicylindrical micelles [26] (Figure 1.5).



Figure 1.5: Schematic showing the effect of bromides in determining the adsorption morphology of surfactant molecules on gold surface. Reproduced with permission from Jaschke, M., *et al.*, "Surfactant aggregates at a metal surface." Langmuir 13.6 (1997): 1381-1384.

Ko, *et al.*, have performed coarse-grained MD simulations to elucidate the adsorption of surfactants on metal surface as a function of the interaction strength of alkyl tails and polar head groups with the surface [27]. They found that the molecules lie flat or stand-up on the surface based on the ratio of interaction strength of their alkyl tails and polar head groups with the surface. This behavior is also observed experimentally in the adsorption study of alkanethiol molecules performed by Poirier, *et al.* [23]. The effect of charged head groups and the counter-ions is however not explained in these studies.

From these findings, it is understood that the adsorption morphology of surfactant molecules is dictated by several factors such as interactions between the alkyl tails, polar head groups, counter-ions, and the surface. A systematic investigation is needed to understand the effect of each of these factors in governing the arrangement of molecules on the surface.

The research described in this dissertation aims at understanding the mechanism of surfactant adsorption on metal-water and air-water interfaces using all-atomistic MD simulations. The effect of charged and uncharged surfactant molecules with different hydrophobic tail lengths is studied. While the adsorption of surfactant molecules on metal-water interfaces is crucial for corrosion inhibition, their adsorption on air-water interfaces is useful for determining their aqueous solubility. Because of amphiphilicity, surfactant molecules have a tendency to adsorb on both hydrophobic and hydrophilic interfaces. For effective corrosion inhibition, strong adsorption of surfactant molecules on metal-water interfaces is desired. However, in an oil-and-gas pipeline, adsorption of surfactant molecules to oil-water and gas-water interfaces is also inevitable [28]. Therefore, a high aqueous solubility of the surfactant molecules is preferred so that the molecules remain available for adsorption to metal-water interfaces.

1.7 Overview of Molecular Dynamics

In classical MD simulations, atomic motion is determined from the time integration of classical equations of motion. Each atom interacts with every other atom via interaction potentials, also known as the forcefields. The interaction potentials are expressed in form of mathematical functions. For instance, charged atoms interact via the Coulombic potential, whereas the interaction between the uncharged atoms is in the form of Van der Waals potential. The forcefields are developed by matching thermodynamic properties obtained from the simulations to the thermodynamic properties obtained from experiments or from the quantum mechanics calculations. The thermodynamic properties, such as pressure, temperature, free energy are obtained from molecular trajectories by invoking the laws of statistical mechanics.

A typical functional form of a forcefield for a molecule is described as [29]:

$$U = \sum_{bonds} k_r (r - r_{eq})^2 + \sum_{angles} k_{\theta} (\theta - \theta_{eq})^2 + \sum_{dihedrals} \frac{v_n}{2} * [1 + \cos(n\Phi - \varphi)] + \sum_{i < j} \left[\frac{A_{ij}}{R_{ij}^{i2}} - \frac{B_{ij}}{R_{ij}^6}\right] + \sum_{i < j} \frac{q_i q_j}{\varepsilon R_{ij}}$$
(1.6)

. .

where U is the total interaction potential of the molecule, and the five terms on the righthand side of the expression denote the bond potential, angle potential, dihedral potential, non-bonded Lennard-Jones interaction potential, and non-bonded Coulombic potential, respectively. k_r , k_{θ} , v_n are force constants; r_{eq} , θ_{eq} are the equilibrium bond lengths, and angles respectively; n is the multiplicity; Φ is the torsion angle of the dihedral, and γ is the phase angle for the torsion angle parameters. The A_{ij} and B_{ij} correspond to the Lennard-Jones potential parameters; q_i and q_j are the charges of the atoms; R_{ij} is the distance between the atoms.

The non-bonded pairwise interaction potential in Equation (1.6) is comprised of the Lennard-Jones potential and the Coulombic potential. Calculation of the Lennard-Jones potential is straightforward because it is a short-range interaction potential, i.e., the interaction becomes negligible beyond a distance of $r \approx 10$ Å. Therefore, for simulation purposes the potential is truncated up to $r \approx 10$ Å. The Coulombic potential, however, is a long-range potential, i.e., the cutoff for the Coulombic interactions is effectively infinite. To avoid the time-consuming calculation of the long-range Coulombic interaction, the computation of the Coulombic potential is done in reciprocal space. Some of the ways for solving long-range Coulombic potential include Ewald summation, and particle-particle particle-mesh (PPPM) method. The computation in Ewald summation scales with the number of particles as N^2 , or at the best as $N^{3/2}$ [30]. The PPPM method, on the contrary, utilizes the Fast Fourier Transforms (FFT) and enables a much faster calculation of the Coulombic interaction. The computation in the PPPM method scales as $N \log N \sim N$ [30]. This method is based on the particle mesh method, in which the charged particles are introduced onto a grid. The Poisson's equations are then solved to solve the potential for this grid. A detailed description of the Ewald summation and the PPPM method is described in [31-33].

A popular forcefield for the organic molecules is the general amber force field (GAFF). GAFF is a widely used forcefield because it has a well-defined bond length, bond angle, partial charge, and Van der Waals parameters for the organic molecules [34]. For these reasons, the forcefield parameters of the organic surfactant molecules studied in this project are obtained from the GAFF.

Some popular force fields for the water molecules are simple point charge model (SPC), extended simple point charge model (SPC/E), and transferable intermolecular potential with three points (TIP3P). Among these, the SPC/E water model is shown to have the most accurate bulk water dynamics and structure when compared to the experimental values [35]. The self-diffusion coefficient, and the radial distribution

functions of SPC/E water model, for example, match well with the experimental values than of the other water models do [35].

The interface force field was developed by the Heinz group to study the interfacial properties of metals such as gold and steel [36, 37]. Though the application of surfactants in this work is for controlling the corrosion of steel pipelines, the simulations in this project are performed on the gold lattice. The interface force field of the steel surface was not developed before this dissertation project was started. Therefore, as an alternative to the iron surface, the gold surface was chosen because just like iron, gold show high polarizability and strong affinity for water [38]. Furthermore, experimentalists have found from QCM measurements that the surfactant molecules show similar adsorption behavior on gold surface as they show on iron surface [39].

MD simulations can be classified into two types – coarse-grained MD simulations and all-atom MD simulations. In coarse grained MD simulations, many atoms of a molecule are grouped together into beads. The purpose of coarse-graining is to reduce the number of atoms or degrees of freedom in an MD simulation without losing the important molecular characteristics. In this way, the numerical calculations become faster and beneficial to study large systems for long time-scales (~1 μ s). In all-atom MD simulations, each atom is defined explicitly. All-atom MD simulations are therefore more accurate but slower than the coarse-grained simulations.

In this work, all-atom MD simulations are performed to study some widely used surfactant molecules in corrosion inhibition. All the MD simulations are performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS). In a fully atomistic MD simulation, the simulations can be performed for a maximum of hundreds of nanoseconds. However, it is understood that the self-assembly of surfactant molecules on metal-water interfaces take several hours [40]. The reason is that in a dense adsorption morphology, the surfactant molecules may experience *diffusional* and energetic barriers to attain the equilibrium configuration. A *diffusional barrier* is any sort of obstruction to the MD simulation system which prevents it to evolve further in the usual simulation time duration. The diffusion barrier is generally overcome by applying an external force (also called *biased force*) to the simulation system or running the simulation for a long time. Therefore, advanced MD simulations are performed which are useful to predict the equilibrium state of the simulation system in an achievable timeframe. In this work, umbrella sampling simulations are performed to calculate the free energies of different states of the simulation system [41]. The equilibrium state is then given by the state with the minimum free energy. The details of the umbrella sampling method are described below.

1.8 Umbrella Sampling Method

An MD simulation proceeds along the direction which minimizes the free energy of the system. If there are multiple free energy basins in the kinetic pathway, then the system is likely to get stuck in one of the free energy basins and never come out of the basin in the simulation timeframe. For instance, in a simulation system comprising of a surfactant molecule near a metal-water interface, the stable state of the surfactant molecule is the state in which the molecule is adsorbed on the metal-water interface. As a result, the molecule may not detach away to diffuse into the bulk aqueous solution. In umbrella sampling, an external biased potential is applied to the system which enables it to come out of the free energy basin and reach other states. In the previous example, a relevant biased potential is a distance-dependent harmonic potential which acts on the surfactant molecule as a function of its distance from the metal surface, $U^b = \frac{1}{2}k(\xi - \xi_0)^2$, where ξ is the distance of the center-of-mass of the molecule from the metal surface, ξ_0 is the set position of the molecule from the metal surface, and k is the force constant. By varying the force constant and the set position of the biased potential, the molecule can be forced to reach to any desired location in the simulation system. The advanced MD simulations are therefore useful to sample the states which are otherwise unreachable in an unbiased MD simulation. By sampling all the states along a kinetic pathway, a free energy profile connecting all those states can be generated based on the probability distributions of the states.

To sample the kinetic pathway along ξ , the pathway is divided into sampling windows of some width, $d\xi$. The biased MD simulations are then performed to individually sample each of these windows. The number and the widths of the sampling windows are chosen such that there is a sufficient overlap of the histograms of probability distributions of the MD simulations of the adjacent windows. A schematic of the histograms of the biased probability distributions, P_i^b and the free energy profile, $A(\xi)$ is shown in Figure 1.6.



Figure 1.6: Schematic showing the histograms of biased probability distributions of individual windows, $P_i^b(\xi)$ and a global free energy profile $A(\xi)$ obtained from unbiased probability distributions.

Upon addition of the biased potential of a window $i, U_i^b(\xi)$ to the unbiased total potential U(r), the modified total potential U'(r) becomes:

$$U'(r) = U(r) + U_i^b(\xi)$$
(1.7)

The unbiased probability distribution in window *i* is given by:

$$P_{i}(\xi) = \frac{\int \exp\left(\frac{-U(r)}{k_{B}T}\right) \delta(\xi'(r) - \xi) d^{N}r}{\int \exp\left(\frac{-U(r)}{k_{B}T}\right) d^{N}r}$$
(1.8)

Similarly, the biased probability distribution in window *i* is given by:

$$P_{i}^{b}(\xi) = \frac{\int \exp\left(\frac{-U(r) - U_{i}^{b}(\xi'(r))}{k_{B}T}\right) \delta(\xi'(r) - \xi) d^{N}r}{\int \exp\left(\frac{-U(r) - U_{i}^{b}(\xi'(r))}{k_{B}T}\right) d^{N}r}$$
(1.9)

Since the bias is applied only to ξ , the Equation (1.9) can be simplified to:

$$P_i^b(\xi) = \exp\left(\frac{-U_i^b(\xi)}{k_B T}\right) * \frac{\int \exp\left(\frac{-U(r)}{k_B T}\right) \delta(\xi'(r) - \xi) d^N r}{\int \exp\left(\frac{-U(r) - U_i^b(\xi'(r))}{k_B T}\right) d^N r}$$
(1.10)

Using Equations (1.8) and (1.10), the unbiased probability can be written as:

$$P_{i}(\xi) = P_{i}^{b}(\xi) \exp\left(\frac{U_{i}^{b}(\xi)}{k_{B}T}\right) * \frac{\int \exp\left(\frac{-U(r) - U_{i}^{b}(\xi)}{k_{B}T}\right) d^{N}r}{\int \exp\left(\frac{-U(r)}{k_{B}T}\right) d^{N}r}$$
$$= P_{i}^{b}(\xi) \exp\left(\frac{U_{i}^{b}(\xi)}{k_{B}T}\right) * \frac{\int \exp\left(\frac{-U(r)}{k_{B}T}\right) \exp\left(\frac{-U_{i}^{b}(\xi)}{k_{B}T}\right) d^{N}r}{\int \exp\left(\frac{-U(r)}{k_{B}T}\right) d^{N}r}$$
$$= P_{i}^{b}(\xi) \exp\left(\frac{U_{i}^{b}(\xi)}{k_{B}T}\right) \langle \exp\left(\frac{-U_{i}^{b}(\xi)}{k_{B}T}\right) \rangle \tag{1.11}$$

Using Equation (1.11) in the expression for free energy, $A_i(\xi) = -k_B T \ln P_i(\xi)$, the free energy can be written as:

$$A_i(\xi) = -k_B T \ln P_i^b(\xi) - U_i^b(\xi) - k_B T \ln \langle exp\left(\frac{-U_i^b(\xi)}{k_B T}\right) \rangle$$
(1.12)

The term $-k_B T \ln \left\langle \exp\left(\frac{-U_i^b(\xi)}{k_B T}\right) \right\rangle$ is a constant value and is undetermined. Mentioning

this term as F_i , the free energy can be simplified to:

$$A_i(\xi) = -k_B T \ln P_i^b(\xi) - U_i^b(\xi) + F_i$$
(1.13)

The biased probability, $P_i^b(\xi)$ is obtained from the biased MD simulation in window *i*. The biased potential, $U_i^b(\xi)$ is also known beforehand. The term F_i is a constant value and does not affect the relative change in the free energy profile in the window *i*. The free energy can therefore be readily evaluated using Equation (1.13). If there are multiple umbrella sampling windows (as shown in Figure 1.6), and if the free energy curves of the windows $A_i(\xi)$ are to be combined to obtain one global free energy curve $A(\xi)$, then the term F_i needs to be calculated for each window. The details of calculation of F_i 's is given in the next section. Moreover, the term F_i can be written in terms of the global unbiased probability distribution, $P(\xi)$ as [42]:

$$\exp\left(\frac{-F_i}{k_B T}\right) = \left\langle \exp\left(\frac{-U_i^b(\xi)}{k_B T}\right) \right\rangle$$
$$= \int P(\xi) \exp\left(\frac{-U_i^b(\xi)}{k_B T}\right) d\xi \tag{1.14}$$

1.9 Weighted Histogram Analysis Method

The weighted histogram analysis method (WHAM) is a method developed by Kumar, *et al.*, to connect the unbiased probability distributions of the umbrella sampling windows and obtain a single unbiased probability distribution for the entire pathway. The global probability distribution, $P(\xi)$ is given by the weighted sum of the individual probability distributions as follows:

$$P(\xi) = \sum_{i}^{windows} w_i(\xi) P_i(\xi)$$
(1.15)

where $w_i(\xi)$ is the weight given to the probability distribution of the window *i*, and $\sum_{i}^{windows} w_i(\xi) = 1.$
The weights $w_i(\xi)$ are chosen in such a way that the statistical error of the unbiased probability is minimized [42]:

$$\frac{\partial \sigma^2(P)}{\partial w_i} = 0 \tag{1.16}$$

From Equations (1.15) and (1.16), one obtains $w_i(\xi)$ as:

$$w_i(\xi) = \frac{N_i \exp\left(\frac{-U_i^b(\xi) + F_i}{k_B T}\right)}{\sum_j N_j \exp\left(\frac{-U_j^b(\xi) + F_j}{k_B T}\right)}$$
(1.17)

where N_i is the total number of steps sampled for the window *i*.

Upon introducing the value of $w_i(\xi)$ in Equation (1.15), the unbiased global probability distribution is obtained:

$$P(\xi) = \frac{\sum_{i}^{windows} N_i P_i(\xi) \exp\left(\frac{-U_i^b(\xi) + F_i}{k_B T}\right)}{\sum_j N_j \exp\left(\frac{-U_j^b(\xi) + F_j}{k_B T}\right)}$$
(1.18)

The $P(\xi)$ and the F_i 's are included in the Equations (1.14) and (1.18). These equations are therefore solved iteratively to obtain $P(\xi)$ and F_i 's. The global free energy profile with respect to ξ is thus generated using the relation $A(\xi) = -k_B T \ln P(\xi)$.

In this work, biasing potentials employed in the umbrella sampling simulations were removed from the configurations by reweighing the probabilities of the configurations using WHAM using the script provided by Grossfield [43].

1.10 Outline of the Chapters

In the second chapter, the free energy profiles of adsorption of surfactant molecules and micelles on metal-water interfaces is determined. The presence of the free energy barrier in adsorption of cationic surfactant micelles is discussed. In the third chapter, a free energy methodology is developed to determine the equilibrium adsorption morphologies of surfactant molecules on metal-water interfaces. The adsorption morphology is determined to be a function of the hydrophobic alkyl length and the nature of polar head groups. The fourth chapter discusses how the aqueous solubility of the surfactant molecules is governed by their hydrophobic tail lengths. The fifth chapter is based on studying the hydration thermodynamics of surfactant molecules of different polar head groups. Based on this understanding, it is proposed that the aqueous solubility of the surfactant molecules can be enhanced by introducing a hydroxyl group to the terminal position of their hydrophobic alkyl tails.

Chapter 2: Free Energy Profiles of Adsorption of Surfactant Micelles at Metal-Water Interfaces^[44]

2.1 Introduction

Adsorption of surfactants on metal surfaces is useful for many technological applications, such as corrosion inhibition [4], improving selectivity in heterogeneous catalysis [45], modulating electrochemical reactions [46] and synthesis of anisotropic metal nanoparticles [47]. It is understood that surfactant molecules adsorb on polar interfaces in different modes, such as with spherical [22], cylindrical [26, 48], and planar morphologies [24, 49-51], thereby altering the interfacial thermodynamic and transport properties [2]. Relationships between molecular properties of surfactant molecules to their favoured morphologies have been analysed via theoretical considerations [18, 52, 53]. An important aspect of the problem is to understand the kinetics of adsorption of surfactants on surfaces. Experimentally, kinetics of adsorption is difficult to study using techniques such as the Quartz Crystal Microbalance (QCM) because the change in the mass associated with adsorbed surfactants is close to the detection limit of QCM, and, there are challenges associated with estimating the adsorbed mass accurately due to presence of hydration water around the polar groups [54, 55]. Spatially-averaged conformations of molecules at interfaces can be studied via Sum Frequency Generation microscopy but these measurements are challenging to perform at metal-water interfaces and in dynamically evolving conditions [56]. The study of kinetics of adsorption of surfactants is complicated by the fact that surfactants aggregate in micelles above the critical micelle concentration (CMC). It is not understood whether the micelles adsorb

^[44] Adapted with permission from H. Singh and S. Sharma, *Free Energy Profiles of Adsorption of Surfactant Micelles at Metal-Water Interfaces*. Mol. Simulat., 2021. 47(5): p. 420-427. Copyright (2020) Taylor and Francis

directly on surfaces or undergo a morphological transformation. Formation of micelles in the bulk aqueous phase is governed by the hydrophobic effect, which may be different near interfaces [57]. In addition, favourable adsorption free energy of individual surfactant molecules will compete with the hydrophobic interactions responsible for the integrity of the micelles. Experiments have reported a change in the adsorption behaviour near the CMC of surfactants, but the underlying reason for it is not known [58]. Previous works have shown that ionic and non-ionic surfactant molecules exhibit different adsorption behaviour on polar solid-water interfaces [59, 60]. One difference in the adsorption behaviour is attributed to the adsorption of counter-ions on charged surfaces, which promotes stronger adsorption of ionic surfactants as compared to non-ionic surfactants [61, 62].

In this work, the adsorption behaviour of cationic and uncharged surfactant molecules and their micelles on metal-water interfaces are compared by calculating their adsorption free energy profiles using molecular simulations. The imidazolinium-based and quaternary ammonium-based molecules (henceforth denoted as imid and quat molecules respectively) are chosen as the cationic surfactants. These molecules are widely employed as corrosion inhibitors in oil and gas pipelines [63, 64]. The structures of these molecules, along with those of uncharged amine-based surfactants (denoted as amine and triamine molecules) studied in this work, are shown in Figure 2.1.



Figure 2.1. Structure of (a) imidazolinium-based (imid), (b) quaternary ammonium-based (quat), (c) amine-based (amine), and (d) amine-based (triamine) surfactant molecules employed in this study. The subscript *n* indicates the length of the alkyl tail. The molecules studied in this work are imid-10, imid-17, quat-10, quat-16, amine-10, triamine-10 which have 10, 17, 10, 16, 10 and 10 carbon atoms in their alkyl tails, respectively.

MD simulations of these surfactants are performed in an explicit aqueous medium and their adsorption free energy profiles are calculated on metal-water interfaces. In addition, the adsorption behaviour of the micelles, treated as rigid bodies, are studied to identify how the adsorption propensity changes in the absence of morphological transitions. To present a complete picture, some of the previously published work on the adsorption behaviour of cationic surfactants are reviewed [65, 66] and then compared with the new simulation results of uncharged surfactants.

2.2 Simulation System and Methods

The simulation system of this work comprises of surfactant molecules, water, counterions and a gold metal surface. Partial charges on the surfactant molecules are calculated from Density Functional Theory (DFT) using B3LYP hybrid functional with 6-31G (d,p) basis set and water as the implicit solvent using Gaussian 09 [67]. Interactions of the surfactant molecules are modelled using the general amber force field (GAFF) [29], a popular force field for organic molecules. The metal surface is represented by six layers of gold atoms arranged in the face-centred cubic structure in the (111) plane with the lattice constant of 4.08 Å. Interactions of gold atoms are modelled using the interface force field developed by Heinz and co-workers [36], which is compatible with GAFF. Chlorides are taken as the counterions and their interactions are modelled using the Joung-Cheatham model [68]. Water molecules are represented by Simple Point Charge Enhanced (SPC/E) model [69]. The metal surface is located at z = 0plane of the simulation box and the opposite face has an athermal surface to keep the system volume constant. The simulation box is periodic in the x and y directions. The simulation box size is 66 Å x 65 Å x 150 Å. Total number of water molecules in the system is 15,575. The canonical ensemble simulations are performed while maintaining the temperature of the system at 300 K using Nose'-Hoover thermostat. A vapor space of \sim 15 Å is kept right below the athermal surface to ensure that the system remains at saturation pressure, and thus the overall system is in the isothermal-isobaric ensemble [70]. In addition to studying surfactants near the metal surface, the aggregation behaviour of the surfactants in bulk aqueous phase is also studied in the absence of a metal surface.

For this system, the simulation box is cubic in dimensions of 65 Å x 65 Å x 65 Å, with periodic boundary conditions in all the three directions. This system has surfactant molecules and their counter-ions in a bath of 9200 water molecules. In case of uncharged surfactant molecules, no counterions are included in the simulation system. A spherical cutoff of 10 Å is chosen for Lennard Jones (LJ) and real space part of Coulombic interactions. The k-space part of Coulombic interactions is computed using the particle-particle particle-mesh (PPPM) method. All MD simulations are performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) software package [71].

2.3 Results and Discussion

In straightforward MD simulations of N quaternary ammonium (quat) and imidazolinium (imid) type surfactant molecules near a metal surface (N = 60), it is observed that a few surfactant molecules adsorb on the metal surface while the remaining molecules aggregate in the aqueous phase as almost spherical micelles [65, 66]. These micelles do not adsorb on the surface during the course of the simulations, which suggests that the adsorption behaviour of unaggregated surfactant molecules is different from their micelles. Therefore, the adsorption behaviour of unaggregated molecules and the micelles is studied by performing independent free energy calculations.

2.3.1 Adsorption Free Energy Profiles in Infinite Dilution

The adsorption free energy profiles of surfactant molecules are calculated in infinite dilution using umbrella sampling [65]. In this calculation, a surfactant molecule is

restrained at a distance ξ from the surface using a harmonic potential. The biasing potential on a configuration *i* restrained at ξ is given by,

$$V_{bias} = k(\xi_i - \xi)^2$$
(2.1)

where ξ_i is the location of the molecule in the configuration *i*. To sample the umbrella sampling windows, the ξ is varied from 3 Å to 25 Å in a series of simulations. For $\xi > 15$ Å, the simulations are performed using the harmonic force constant, $k = 5 \text{ kcal/mol/}\text{Å}^2$ and with ξ varying in increments of 1 Å. For $\xi \leq 15$ Å, the simulations are performed with the force constants, k = 10, 25 and 50 kcal/mol/Å² and with ξ varying in increments of 0.5 Å. Larger values of k are needed for $\xi \le 15$ Å because the molecules show a strong tendency to adsorb and thus more restraining force is needed to adequately sample these locations. For each value of ξ , an equilibrium run of 20 ns is performed, which is followed by a production run of 40 ns. The free energy profiles are generated using the Weighted Histogram Analysis Method (WHAM) [65]. Figure 2.2 shows the resultant adsorption free energy profiles of quat-10 and quat-16 molecules in infinite dilution on the metal surface [72]. It is observed that the surfactant molecules adsorb strongly ($\Delta G \approx$ - 35 k_BT) without experiencing any free energy barrier. Similar adsorption free energy profiles have been reported for the imid molecules [65]. The inset image shows a snapshot of a quat-10 molecule in the adsorbed state. It is seen that the most favourable configuration of the molecule is to lie flat on the surface.



Figure 2.2. Adsorption free energy profiles of quat-10 and quat-16 molecules in infinite dilution on a gold lattice; inset: equilibrium adsorbed configuration of the quat-10 molecule. Error bars are calculated by generating three independent free energy profiles. The centers of metal atoms in the topmost layer of the metal surface are located at $\xi = 0$ Å. Water molecules are represented in cyan color and the gold lattice is represented by orange beads. The blue bead represents the counterion, chloride.

2.3.2 Adsorption Free Energy Profiles of Surfactant Micelles

As discussed above, the straightforward MD simulations have revealed that the surfactant molecules aggregate in micelles in the aqueous phase. To study their aggregation tendency, simulations of these molecules in the bulk aqueous phase are performed in the absence of a metal surface. The MD simulations of imid and quat type surfactants show that these molecules aggregate in micelles of 18-19 molecules. It is observed that a larger micelle is not formed even when a simulated annealing is

performed from 400 K to 300 K in steps of 10 K [65, 66]. From the radius of gyration tensor of these micelles, the asphericity values are found to be close to 0.15, indicating that these micelles are nearly spherical and have a radius of ~ 15 Å [65, 66]. The uncharged molecules also form spherical micelles. The asphericity values of amine-10 and triamine-10 micelles, each comprising of 18 molecules are 0.13 and 0.15, respectively. Unlike the cationic surfactants, the uncharged molecules are able to form micelles of size larger than 18 molecules. The inability of cationic surfactants to form larger micelles is probably due to the unfavourable Coulombic interactions between the surfactant molecules [38]. The micelles of uncharged surfactants have a higher packing density. The number densities (number of heavy atoms per unit volume of micelle) of amine-10 and triamine-10 micelles comprising of 18 molecules are 0.37 heavy atoms/Å³ and 0.33 heavy atoms/Å³, respectively, whereas those of imid-10 and quat-10 micelles are 0.28 heavy atoms/Å³ and 0.26 heavy atoms/Å³, respectively [38]. Figure 2.3 shows snapshots of the different surfactant micelles formed in the simulations. The polar head groups can be seen pointing outwards towards the aqueous phase. This result is supported in Figure S1 (Supporting Information, Appendix A), which shows the distribution of polar head groups as a function of their distance from the centre of mass of the micelles.



Figure 2.3. Snapshots of (a) an imid-10 micelle, (b) an imid-17 micelle, (c) a quat-10 micelle, (d) a quat-16 micelle, (e) an amine-10 micelle, and (f) a triamine-10 micelle, respectively. Red beads represent the polar head groups, and the yellow beads represent the alkyl tails.

2.3.2.1 Micelles of Cationic Surfactants. To calculate the free energy profiles of adsorption of micelles, one micelle is placed in the aqueous phase at different distances from the metal surface, ξ . The micelle is restrained close to ξ via the above-described umbrella sampling methodology but with the modification that now the biasing potential (Equation (2.1)) is applied to the centre of mass of the micelle. In these simulations, for $\xi > 25$ Å, the harmonic force constant, k = 5 kcal/mol/Å² is used and ξ is varied in

increments of 1 Å. For $\xi \le 25$ Å, k = 10, 25, and 50 kcal/mol/Å² are employed with ξ varied in increments of 0.5 Å. At each location, an equilibrium run of 40 ns is followed by a production run of 40 ns, except at distances close to the surface ($\xi \le 20$ Å), wherein a longer equilibrium run (~ 100 – 200 ns) is needed to attain equilibrium configuration of the micelle. Figure 2.4 shows the adsorption free energy profiles of imid-17 and quat-10 micelles [66].



Figure 2.4. Free energy profiles of the adsorption of (a) imid-17, and (b) quat-10 micelles. Error bars are calculated by generating three independent free energy profiles. Adapted with permission from Singh and Sharma [28]. Copyright (2020) American Chemical Society.

It is observed in Figure 2.4 that the cationic micelles experience a repulsion from the metal surface even up to $\xi = 50$ Å. Since the radius of the micelles is ~15 Å, this is a

long-range repulsion. This long-range repulsion is attributed to the presence of a solvation shell of counter-ions and water molecules surrounding the micelle, which interacts with the adsorbed layers of water on the metal surface [65, 66] (kindly refer Figures S2, S3, S4 (Supporting Information, Appendix A) that show the radial distribution functions of counterions around the polar head, water molecules around the counterions and the adsorbed layers of water on the metal surface). Once this barrier is overcome, Figure 2.4 shows that the free energy of adsorption of the micelles is favourable. It is observed that the micelles adsorb strongly by disintegrating at the metal surface. The complete disintegration of the micelles occurs in a timescale of ~200 ns [66]. Figure 2.5 shows snapshots of the imid-17 micelle obtained from an unbiased simulation at different times when the micelle is initially placed on the metal surface. The snapshots show that the imid-17 micelle completely disintegrates on the metal surface over time. Upon disintegration, the constituent molecules of the micelle lie flat on the metal surface.

It is to be noted that the free energy profiles in Figure 2.4 are plotted only up to 10 k_BT in order to show the long-range free energy barrier clearly. The true minimum of the free energy profiles would be a much lower value, approximated to be the summation of the adsorption free energies of all the constituent molecules.



Figure 2.5. Unbiased MD simulation showing the adsorption and disintegration of imid-17 micelle on the metal surface. Adapted with permission from Singh and Sharma [28]. Copyright (2020) American Chemical Society.

Disintegration of micelles at metal-water interfaces can be understood by comparing the free energy associated with the formation of a micelle in the bulk phase ($\Delta G_{\text{micellization}}$) with the free energy of the molecules adsorbing on the surface ($\Delta G_{\text{adsorption}}$). The $\Delta G_{\text{micellization}}$ of an imid-10 micelle comprising of N = 18 molecules is previously calculated to be ~ -68 k_BT [72]. $\Delta G_{\text{adsorption}}$ for these molecules will be $N \times$ (-30) $k_BT \sim$ -540 k_BT [65]. Hence, $\Delta G_{\text{adsorption}} \ll \Delta G_{\text{micellization}}$, which suggests that the micelle has a tendency to disintegrate upon adsorption on the metal surface. Experiments have reported that quaternary ammonium surfactants adsorb on a gold surface in the lying-down configuration, similar to these simulation results [66].

To prove that the disintegration of the micelles is responsible for their strong adsorption, the adsorption free energy profiles of the micelles are calculated by treating them as rigid bodies. A rigid micelle is created by selecting a configuration of the nonrigid micelle which has the same values of asphericity and squared radius of gyration as the averaged values of the non-rigid micelle in the bulk aqueous phase. In a rigid micelle, all intra-molecular interactions are set to zero. The external forces and torques act on the centre of mass of the micelle. Hence, a rigid micelle cannot deform like the non-rigid micelle. Free energy profiles of adsorption of the rigid and the non-rigid imid-10 and quat-16 micelles are shown in Figure 2.6 [66].



Figure 2.6. Free energy profiles of adsorption of the rigid and the non-rigid micelles of (a) imid-10, and (b) quat-16 molecules. The error bars are determined from three independent free energy profiles. Adapted with permission from Singh and Sharma [28]. Copyright (2020) American Chemical Society.

It is observed in Figure 2.6 that there is a long-range free energy barrier to adsorption of the rigid micelles, as in the case of the non-rigid micelles. However, the adsorption free energy of the rigid micelles is only metastable. This confirms the assertion that when the micelles do not disintegrate, they only have a weak tendency to adsorb on the metal surface. Another difference that is noticed is that the free energy barrier of the rigid micelles is larger and has a peak at 18 Å as opposed to 22 Å in the case of the non-rigid micelles. At this peak, the micelles partially lose their solvation shell because of their proximity to the metal surface. In the case of non-rigid micelles, however, this loss in energetics is compensated by the rearrangement of the molecules comprising the micelle. The absence of this rearrangement in the case of rigid micelles results in a larger free energy barrier.

Free energy profiles for the rigid micelles are only ascertained up to 15.5 Å from the metal surface because that is the closest distance that these micelles can attain owing to their rigidity. Figure 2.7 shows the equilibrium adsorbed morphology of a (a) rigid micelle and (b) a non-rigid micelle on the metal surface. The non-rigid imid-17 micelle is disintegrated with its molecules lying flat on the surface.



Figure 2.7. Snapshot of (a) a rigid quat-16 micelle, and (b) a non-rigid imid-17 micelle adsorbed on the metal surface at equilibrium. Water molecules are not shown for clarity. Adapted with permission from Singh and Sharma [28]. Copyright (2020) American Chemical Society.

2.3.2.2 Micelles of Uncharged Surfactants. In the previous section, it is shown that the cationic micelles experience a long-range free energy barrier to adsorption because of the presence of a large corona of counter-ions and water molecules in their

solvation shell. In this section, the adsorption free energy profiles of micelles of uncharged molecules that do not have a corona of counterions are discussed. The adsorption behaviour of amine-10 and triamine-10 micelles are studied (Figure 2.3). Each micelle that is studied comprises of 18 molecules. Figure 2.8 (a) shows the adsorption free energy profiles of the non-rigid and the rigid amine-10 micelles, and Figure 2.8 (b) shows the adsorption free energy profile of the non-rigid triamine-10 micelle.



Figure 2.8. Free energy profiles of the adsorption of (a) the rigid and the non-rigid amine-10 micelles, and (b) the non-rigid triamine-10 micelle. The error bars are determined from three independent free energy profiles.

Interestingly, it is observed that there is no free energy barrier to the adsorption of the uncharged micelles, which suggests that the free energy barrier in the case of cationic micelles is due to the corona of the counterions. Figure 2.8 (a) also shows that the rigid

amine-10 micelle has a weaker adsorption free energy as compared to the non-rigid micelle, highlighting that the disintegration of the micelles is responsible for their strong adsorption. The free energy profiles for the non-rigid micelles is plotted only up to $14 k_B T$ in order to clearly highlight the difference between the profiles of the rigid and the non-rigid micelles. These free energy profiles suggest that the adsorption of uncharged micelles is kinetically favoured over the adsorption of cationic surfactants on uncharged metal surfaces.

Figure 2.9 depicts the equilibrium morphology of the uncharged micelles in the absorbed state after an unbiased simulation run of 200 ns. The amine micelle is disintegrated with its molecules lying flat on the surface. On the other hand, the triamine micelle is disintegrated with its molecules standing up on the surface, with most of the polar head groups (17 out of 18) pointing down towards the metal and the hydrophobic tails pointing up towards the bulk aqueous phase. Figure S5 (Supporting Information, Appendix A) shows the average orientation of the molecules in the adsorbed state of the micelles.

The difference between an amine and a triamine molecule is their polar head group. The triamine molecule has three amine groups which makes it a strongly polar group as compared to the amine molecule, which has only one amine group. The orientation of the molecules on the surface depends upon the strength of interaction of their polar head groups with the metal surface [53]. The triamine molecules prefer to stand-up on the surface because in the lying-down configuration, the interaction of the head group with the surface is weaker as only one nitrogen can be in contact with the surface. The kinetics of adsorption of the triamine micelle suggests how the islands of molecules standing-up on the surface, as reported in the experiments may form during the adsorption process.



Figure 2.9. Snapshot of (a) an amine-10 micelle, and (b) a triamine-10 micelle disintegrated on the metal surface. Amine-10 molecules lie flat, while the triamine-10 molecules stand up on the surface.

2.4 Conclusions

In this work, the adsorption behaviour of surfactants at metal-water interfaces are studied using atomistic simulations. It is found that the adsorption behaviour depends on the aggregated state of the surfactants. In the unaggregated state, the molecules have a strong tendency to adsorb without any free energy barrier. Micelles of cationic surfactants experience a long-range free energy barrier to adsorption on an uncharged metal surface because they have a corona of counterions surrounding the micelles which gets disturbed as the micelles approach the surface. Uncharged micelles, devoid of a corona of counterions show a barrierless adsorption free energy profile. In addition, it is shown that the micelles adsorb strongly on to the metal surface upon disintegration. Rigid micelles, which cannot disintegrate, show only a weak tendency towards adsorption. Finally, it is shown that in the disintegrated state, the surfactant molecules can attain a lying-down configuration or a standing-up configuration, depending upon the strength of interaction of their head groups with the metal surface.

Chapter 3: Determination of Equilibrium Adsorbed Morphologies of Surfactants at Metal-Water Interfaces Using a Modified Umbrella Sampling-based

Methodology^[73]

3.1 Introduction

As mentioned previously, understanding surfactant – metal interactions are important for numerous applications. Surfactants have a strong affinity to adsorb at metal-water interfaces and display a rich adsorption behavior as a function of their molecular properties. As an example, increasing the alkyl tail length of trimethyl ammonium bromide (C_nTAB) during the C_nTAB-mediated synthesis of gold nanorods increases the aspect ratio of the nanorods, presumably because longer alkyl tails cause stronger inter-tail packing in the adsorbed C_n TAB layer [74]. In the synthesis of gold nanorods, increasing the size of the polar head of surfactants has been shown to enhance the anisotropy of the nanorods [75]. Indeed, direct scanning of morphologies of adsorbed surfactants on metallic and polar surfaces has revealed the formation of planar [24], spherical [76] and cylindrical micelles [26, 77]. The formation of these morphologies is understood to be dictated by molecular geometry [18], lateral hydrophobic interactions [27, 38, 78-80] as well as coulombic interactions between the polar head, surface, and the counterions [26, 76, 80]. For instance, based on the differences in the atomic force microscopy (AFM) images, Jaschke, *et al.*, postulate that the adsorption of $C_{14}TAB$ molecules on gold is mediated by Br⁻ counterions resulting in cylindrical micelles, while C16TAOH and sodium dodecyl sulfate (SDS) adsorb as hemicylindrical micelles due to the interactions between the alkyl tails and the surface [26]. Using sum frequency

generation (SFG) microscopy, Khan, *et al.*, show that the cationic alkyl dimethyl benzyl ammonium bromide surfactants with four carbon long (C₄) alkyl tails adsorb in random orientations on gold surface, whereas those with C_{12} alkyl tails adsorb in a planar SAM, thereby highlighting the importance of lateral hydrophobic interactions between the alkyl tails in the adsorption [81]. It should be noted that in these studies, the AFM and SFG microscopy have resolutions of, at best, tens of nanometers, and therefore are unable to resolve the morphologies at the atomistic scale.

While it is recognized that multiple factors influence the adsorption morphology of surfactants at metal-water interfaces, no unifying guiding principle to predict these morphologies has emerged so far. One reason is that the organization of surfactant molecules in densely packed adsorbed morphologies is characterized by diffusional and/or energetic barriers, and the existing molecular simulation methodologies do not allow efficient sampling of the formation of these morphologies. Previous simulation studies have attempted to navigate this problem by initializing the simulations with surfactants arranged in a planar SAM on surfaces [81-85]. This approach is sub-optimal as it introduces a bias towards certain configurations and does not allow calculation of the free energy of adsorbed morphologies to determine which is most stable. In this work, a new umbrella sampling-based [41] free energy sampling methodology is introduced that allows study of densely packed adsorbed morphologies. Using this methodology, the most stable adsorbed morphology of different surfactant molecules is determined.

3.2 Theory and Simulation Methodology

Molecular dynamics (MD) simulations are performed to study the adsorption behavior of cationic quaternary ammonium-based molecules of alkyl tail lengths C₄ and C₁₂ [henceforth referred to as quat-4 and quat-12 respectively], charge-neutral decanethiol, and anionic phosphate monoester molecules of C₁₂ alkyl tail length [henceforth referred to as pe-12] at a gold-water interface. These molecules are widely used for corrosion inhibition in the oil-and-gas industry [13, 86]. The structures of these molecules are shown in Figure 3.1 (a, b, c). In addition, the adsorption behaviors of mixtures of these molecules are studied. First, the free-energy methodology that allows sampling of high-density adsorption morphologies is introduced.

The equilibrium adsorption morphology of surfactant molecules is the one that has the lowest free energy amongst the other morphologies. A collective variable needs to be devised along which different adsorption morphologies can be sampled. For this purpose, an *adsorption number* function is defined by:

$$\xi(\mathbf{z}, z_o, n, m) = \sum_{i=1}^{N} \frac{1 - (z_i/z_o)^n}{1 - (z_i/z_o)^m}$$
(3.1)

where, z_i is the distance of polar head of the surfactant molecule identified by the subscript *i* from the top layer of the metal lattice; *z* represents the set of z_i for all *i*; z_0 is the cut-off distance that decides the point of inflection of the function; *n* and *m* are integers (n < m) that control the long-range behavior and stiffness of the function; and *N* is the total number of surfactant molecules in the system. As $z \to 0$, $\xi(z, z_o, n, m) \to N$ and as $z \to \infty$, $\xi(z, z_o, n, m) \to 0$. Therefore, $\xi(z, z_o, n, m)$ maps the number of adsorbed molecules to a continuous and differentiable function with the range of (0, N). The departure from using integers (number of adsorbed molecules) to using a continuous and differentiable function to represent the adsorbed amount is advantageous as one can define a biased umbrella sampling potential based on $\xi(\mathbf{z}, \mathbf{z}_o, n, m)$ that does not change stepwise and therefore the biasing forces are well-defined. For this system, $\mathbf{z}_0 = 18$ Å, n = 2, and m = 4. For ease of representation, the adsorption number function is simply referred to as ξ . For a single molecule (N = 1), the dependence of ξ on z is shown in Figure 3.1 (d).



Figure 3.1. Molecular structures of (a) cationic quat surfactants (n = 3 and 11 for quat-4 and quat-12 respectively), (b) alkanethiol surfactant (n = 9 for decanethiol), and (c) phosphate monoester surfactant (n = 11 for pe-12). (d) $\xi(z, z_o, n, m)$ as a function of z for N = 1. The values of other parameters are $z_0 = 18$ Å, n = 2, and m = 4. (e) Initial configuration of the simulation system with quat-12 molecules near the gold-water

interface. The red beads represent the aromatic rings, the yellow beads represent the alkyl tails of the surfactant molecules, the blue beads represent the bromide counter-ions, and the cyan dots represent water molecules. Gold atoms are shown as orange beads.

To sample different adsorbed amounts, an umbrella sampling bias potential is applied based on ξ given by, $U(\xi, \xi_o) = \frac{1}{2}k(\xi - \xi_o)^2$, where *k* is the force constant; ξ is the value of the adsorption number function for a configuration; ξ_o is the set value of the adsorption number function for an umbrella sampling window. After sampling all the windows, the free energy profile as a function of ξ is generated by applying the weighted histograms analysis method [87]. The umbrella sampling is performed using the COLVARS package in LAMMPS [71, 88]. The initial configurations of the MD simulation are generated by inserting the surfactant molecules at random locations and orientations in the simulation box [Figure 3.1 (e)].

The simulation box is periodic in the X and Y directions, and a metal surface comprising of six layers of gold atoms arranged in (111) Miller index occupies the z = 0face of the simulation box. The opposite face of the simulation box has an athermal reflective wall. A vacuum region of ~10 Å is kept above the water column to ensure that the system pressure remains at the saturation pressure corresponding to T = 300 K [70]. To prevent the surfactant molecules from accumulating at the air-water interface [81], a barrier is placed in form of a wall at ~15 Å below the air-water interface, which is permeable to the water molecules but not to the surfactant molecules and counterions. The top three layers of the gold lattice are mobile, whereas the bottom three layers are immobile. Area of the gold surface exposed to the aqueous medium, equal to the x-ydimensions of the simulation box, is 49.04 Å x 49.97 Å. Partial charge on each atom of a surfactant molecule is calculated from density functional theory (DFT) calculations using B3LYP hybrid functional theory with 6-31G (d, p) basis set in implicit water using Gaussian 16 [89]. Interaction potential parameters of surfactant molecules are obtained from the General Amber Force Field (GAFF) [29]. Water molecules are represented using the extended simple point charge (SPC/E) model [90]. Interaction potential parameters of gold atoms are obtained from the interface force field developed by Heinz and co-workers [36]. Bromide and sodium ions are introduced as the counter-ions for the cationic and the anionic surfactant molecules respectively, and their interaction potential parameters are obtained from the Joung and Cheatham's model [68]. The overall system is charge-neutral. The gold-thiol interaction is obtained from a previous work [91]. The cutoff distances for Lennard-Jones and short-range Coulombic interactions are taken as 10 Å. The long-range Coulombic interactions are calculated using the particle-particleparticle-mesh (pppm) method. The simulations are performed in the canonical ensemble (constant number of particles N, volume V, and temperature T) at a temperature of 300 K.

The above-described umbrella sampling methodology is employed to study the equilibrium adsorption morphology of five different surfactant systems — quat-12, quat-4, decanethiol, an equimolar mixture of quat-12 and pe-12, and an equimolar mixture of quat-12 and quat-4. All simulations are performed with the same molar concentration of surfactants. In each umbrella sampling window, the system is equilibrated for the first 40 ns, and the next 40 ns are used for free energy calculations. More details of the umbrella

sampling parameters, and simulation system sizes are discussed in the Supporting Information (Appendix B).

3.3 Results and Discussion

3.3.1 Adsorption of Quat-12 Molecules

The free energy profile, ΔF as a function of ξ of quat-12 molecules is shown in Figure 3.2 (a).



Figure 3.2. (a) Free energy profile, ΔF as a function of the adsorption number function, ξ of quat-12 molecules near the metal-water interface. The inset image shows the top view of the equilibrium adsorption morphology corresponding to the free energy minimum. (b)

Side view of the equilibrium adsorption morphology. Error bars in (a) are obtained from three independent estimates of the free energy profile.

The minimum in the ΔF is observed at $\xi = 27.5$, which corresponds to the most stable adsorbed morphology. The equilibrium morphology comprises of a layer of molecules lying flat onto the metal surface and on top of it, a hemispherical micelle of surfactants is adsorbed [Figure 3.2 (b)]. The top view shows that the metal surface is nearly fully covered by the quat-12 molecules. Due to the long alkyl tails, quat-12 molecules have strong hydrophobic interactions amongst themselves. The ΔF is shown only for the range of $18 < \xi < 43$, as beyond this range, the $\Delta F > 100 k_B T$. A long (275 ns) unbiased MD simulation at $\xi = 27.5$ does not drift away to a significantly different value of ξ , but fluctuates in between 24 $\lesssim \xi \lesssim$ 27.5 [Figure S1, Supporting Information (Appendix B)]. This fluctuation is because there is a neighboring free energy basin at $\xi =$ 24 with a small free energy barrier of ~4 k_BT at $\xi = 26.25$. This free energy barrier is associated with a micelle approaching the surface from the bulk aqueous phase [Figures S2, S3, Supporting Information (Appendix B)]. In a previous work, it is shown that a cationic micelle encounters a free energy barrier to adsorption when it approaches the metal surface [44, 66]. In the bulk phase, quat-12 molecules are stable in a micellar state, due to the favorable micellization free energy [72].

Figure 3.3 (a) shows distribution of orientation of the alkyl tails of adsorbed quat-12 molecules with respect to the surface normal in the equilibrium adsorbed morphology. The angle θ is defined as the angle between the end-to-end vector of the alkyl tails and the surface normal. The cartoons shown in the inset explain the various features of the distribution. The peak at $\theta \approx 90^{\circ}$ corresponds to the adsorbed monolayer of lying-down molecules. The broad plateau for $\theta \in (90^{\circ}, 180^{\circ})$ shows that the adsorbed micelle is hemispherical in shape as shown in the inset. Therefore, in the equilibrium adsorbed morphology, the quat-12 molecules adsorb as a hemispherical micelle sitting on top of a monolayer of lying-down molecules. There are ~30 quat-12 molecules adsorbed in the equilibrium, with ~16 molecules lying flat onto the surface and ~14 molecules arranged in the hemispherical micelle. Figure 3.3 (b) shows distribution of the orientation of the aromatic rings of the adsorbed quat-12 molecules with respect to the surface normal, where φ is the angle between the surface normal and the vector normal to the plane of the aromatic ring. The peak at $\varphi < 15^{\circ}$ is due to the lying-down molecules wherein the aromatic ring is parallel to the surface. The uniform distribution for $\varphi \in (30^{\circ}, 90^{\circ})$ is from the hemispherical micelle.



Figure 3.3. Distribution of the orientation of (a) alkyl tails, and (b) aromatic rings of adsorbed quat-12 molecules on the metal surface. In (a), θ is the angle between end-toend vector of the alkyl tails and the surface normal. In (b), φ is the angle between vectors normal to the aromatic ring and the surface normal. The distribution profiles are normalized by $\langle N \rangle \sin(\theta)$ and $\langle N \rangle \sin(\varphi)$ respectively, where $\langle N \rangle$ is the ensemble-average number of adsorbed molecules. A molecule is considered as adsorbed when its center-of-mass lies within one molecular length (~23 Å) from the metal surface. The height of the adsorbed hemispherical micelle is around one molecular length. In (b), a large peak for $0^{\circ} < \varphi < 15^{\circ}$ indicates that for the molecules lying down on the surface, the aromatic rings are parallel to the metal surface. The uniform distribution observed for $30^{\circ} < \varphi < 90^{\circ}$ is from the adsorbed hemispherical micelle. The peak of the distribution below $\varphi < 11^{\circ}$ goes to a very large value (>>0.1) and is not shown in (b) in order to enable visibility of the small distribution in between $30^{\circ} < \varphi < 90^{\circ}$.

Due to diffusive barriers, the equilibrium adsorbed morphology is not attained in an unbiased MD simulation [Figure S4 (a), Supporting Information (Appendix B)]. Other morphologies, such as a monolayer of molecules lying parallel to the surface [Figures S4 (b), Supporting Information (Appendix B), with $\xi_0 = 20$], or a monolayer of molecules tightly packed and standing-up on the surface [Figure S4 (c), Supporting Information (Appendix B), with $\xi_0 = 47$] are free-energetically unfavorable. [Also refer to Table S1, Supporting Information (Appendix B), for comparison of ensemble-average energies of the equilibrium configuration and standing-up configuration]. The proposed umbrella sampling methodology allows sampling of adsorbed configurations as a function of the adsorbed amount measured by ξ . In the Figure S10 [Supporting Information, Appendix B], the free energy profiles are plotted with respect to another order parameter, *N* which is the number of adsorbed molecules in integers. A similar trend in the free energy profile confirms that ξ is strongly correlated to *N*. There may be additional order parameters needed to capture the kinetic pathways of the adsorption process, along which one may encounter large free energy barriers associated with the adsorption. Ideally, additional order parameters can be incorporated in this methodology, but that requires more extensive sampling. The current methodology overcomes the long diffusional timescales that are associated with the surfactant micelles and their rearrangement on the surface.

3.3.2 Adsorption of Quat-4 Molecules

Figure 3.4 (a) shows the free energy profile, ΔF of quat-4 molecules as a function of ξ . The equilibrium morphology corresponding to the free energy minimum at $\xi = 24$ is shown in Figure 3.4 (b). Unlike the quat-12 molecules, quat-4 molecules do not aggregate in the bulk to form micelles because of their smaller alkyl tails. The quat-4 molecules adsorb by lying flat onto the metal surface, and do not completely cover the surface. There are ~19 quat-4 molecules adsorbed in the equilibrium adsorbed morphology. The sparse adsorption of quat-4 molecules is attributed to the accumulation of charged head groups on the surface, which makes further adsorption unfavorable. The distributions of the orientation of alkyl tails and the aromatic rings of the adsorbed molecules with respect to the surface normal are shown in Figure S5 [Supporting Information (Appendix B)].



Figure 3.4. (a) Free energy profile, ΔF as a function of the adsorption number function, ξ of quat-4 molecules near the metal-water interface. The inset image shows the top view of the equilibrium adsorption morphology corresponding to the free energy minimum. (b) Side view of the equilibrium adsorption morphology. Error bars in (a) are obtained from three independent estimates of the free energy profile.

From the contrasting adsorption behavior of quat-12 and quat-4 molecules, it is concluded that the accumulation of charge limits the adsorption of cationic surfactants. In

the case of quat-12 molecules, the strong hydrophobic interactions between the alkyl tails result in a configuration wherein a hemispherical micelle adsorbs on top of a monolayer of molecules lying parallel to the surface. Interestingly, the morphology with micelles of adsorbed surfactant molecules atop a monolayer of molecules lying parallel to the surface have been proposed before based on AFM imaging [26]. Surfactant molecules with small alkyl tails (< C_6) show a significantly reduced corrosion inhibition efficiency [92, 93]. This result is rationalized by the findings that quat-4 molecules only partially cover the surface.

3.3.3 Adsorption of Decanethiol Molecules

Next, the adsorption behavior of decanethiol molecules is studied that are chargeneutral and have a long alkyl tail. The thiol group has a strong affinity for the metal surface. The ΔF of decanethiol molecules as a function of ξ is shown in Figure 3.5 (a) and a side-view snapshot of the equilibrium adsorbed morphology is shown in Figure 3.5 (b). Decanethiol molecules display a much denser packing in the adsorbed state as compared to the cationic molecules. The number of adsorbed decanethiol molecules is ~196 as compared to ~30 molecules in the quat-12 system. A bilayer morphology is observed in which the first layer comprises of the molecules aligned in a standing-up orientation on the surface and the second layer is comprised of the molecules aligned parallel to the surface. The number of decanethiol molecules is ~147 in the first adsorbed layer and ~49 in the second adsorbed layer. The bilayer adsorption of decanethiol has also been reported in electrochemical impedance spectroscopy experiments [94]. The distribution of the orientation of molecules in the adsorbed bilayer is shown in Figure S6 [Supporting Information (Appendix B)]. The dense packing of decanethiol molecules on the metal surface is explained by the lack of charge accumulation, strong thiol-metal interactions, and favorable hydrophobic interactions between the alkyl tails.



Figure 3.5. (a) Free energy profile, ΔF as a function of the adsorption number function, ξ of decanethiol molecules. The inset image shows the top view of the equilibrium adsorbed morphology corresponding to the free energy minimum at $\xi = 161$. (b) Side view of the equilibrium adsorbed morphology. Error bars in (a) are obtained from three independent estimates of the free energy profile. The red beads represent the thiol groups, and the yellow beads represent the alkyl tails of the molecules.

3.3.4 Adsorption of Equimolar Mixture of Quat-12 and Pe-12 Molecules

Since the accumulation of charge is identified as a factor that limits adsorption, a mixture of cationic and anionic surfactants may show a synergistic improvement in adsorption. To study this, the adsorption behavior of an equimolar mixture of cationic quat-12 and anionic pe-12 molecules is examined [refer to Figure 3.1 for their structures]. Figure 3.6 shows the ΔF and the corresponding equilibrium adsorbed morphology of this system. Interestingly, a significantly greater number of adsorbed molecules is observed: \sim 43 as compared to \sim 30 in a pure quat-12 system. Electrochemical measurements have previously shown that quat-14 and pe-12 molecules individually show a similar adsorption tendency [95]. This simulation result suggests that, as hypothesized, a mixture of cationic and anionic surfactant molecules shows synergistic improvement in the adsorption. Indeed, synergistic improvements in adsorption have been observed experimentally upon mixing phosphate monoester molecules with the cationic imidazolinium-based/quaternary ammonium-based molecules [96, 97]. The presence of oppositely charged molecules on the surface reduces the amount of charge accumulation and favors a denser adsorption morphology [98]. The distribution of the orientation of alkyl tails of the adsorbed molecules with respect to the surface normal are shown in Figure S7 [Supporting Information (Appendix B)].


Figure 3.6. (a) Free energy profile, ΔF as a function of the adsorption number function, ξ of an equimolar mixture of quat-12 and pe-12 molecules near the metal-water interface. The inset image shows the top view of the equilibrium adsorbed morphology corresponding to the free energy minimum. (b) Side view of the equilibrium adsorbed morphology. Error bars in (a) are obtained from three independent estimates of the free energy profile. The red and green beads represent the head groups of quat-12 and pe-12 molecules respectively, and the yellow beads represent the alkyl tails of both the molecules. The blue and black beads represent the counter-ions: bromide and sodium ions respectively. It is noteworthy that the bromide ions are disfavored from associating with the quat-12 molecules, the pe-12 molecules being favored instead. The bromide and sodium ions are more water solvated in the bulk aqueous phase than they are at the metal-

water interface [also refer to Table S1, Supporting Information (Appendix B), for comparison of ensemble-average energies of the equilibrium configuration and standingup configuration]. Therefore, the ions prefer to stay in the bulk aqueous phase, while the surfactant molecules mostly prefer to stay at the metal-water interface.

3.3.5 Adsorption of Equimolar Mixture of Quat-12 and Quat-4 Molecules

The adsorption behavior of an equimolar mixture of quat-12 and quat-4 molecules is also studied. Figure 3.7 shows the ΔF and the corresponding equilibrium adsorbed morphology of this system. It is observed that the quat-12 molecules adsorb in the aggregated state but are not organized in a hemispherical micelle as before [Figure S8 (a), Supporting Information (Appendix B)]. The quat-4 molecules adsorb by lying parallel onto the surface [Figure S8 (b), Supporting Information (Appendix B)]. No synergistic improvement in the adsorption behavior in this mixture is observed.



Figure 3.7. (a) Free energy profile, ΔF as a function of the adsorption number function, ξ of an equimolar mixture of quat-12 and quat-4 molecules near the metal-water interface. The inset image shows the top view of the equilibrium adsorption morphology corresponding to the free energy minimum at $\xi = 26$. (b) Side view of the equilibrium adsorption morphology. Error bars in (a) are obtained from three independent estimates of the free energy profile. The red beads represent the aromatic rings of the quat molecules. The alkyl tails of two kinds of quat molecules are differentiated by yellow and brown beads, each representing the tails of quat-12 and quat-4 molecules respectively. Figure S18 [Supporting Information (Appendix B)] compares the ΔF of the mixture of quat molecules with the profiles of pure quat-12 and quat-4 molecules. The ΔF of the mixture shows a broader range of ξ at the minimum, implying that many different

adsorbed configurations are possible. The distributions of the orientation of alkyl tails of the adsorbed molecules with respect to the surface normal are shown in Figure S8 [Supporting Information (Appendix B)].

For inhibiting corrosion, the ability of the adsorbed surfactant molecules to exclude water from the metal surface is desired [21]. In Figure 3.8, the density profiles of water in absence and presence of the adsorbed morphologies of all the five surfactant systems are compared. It is observed that decanethiol molecules, due to their strong packing in the adsorbed state, are the most efficient in excluding water from the interface. To estimate corrosion protection from the adsorbed surfactant morphologies, the number of water molecules present in the vicinity of the surface is calculated as the area under the density profiles. Corrosion is caused by the reduction of the oxidizing species, such as H⁺ and O_2 , at the metal surface. For corrosion to continue, the diffusion of the oxidizing species from the bulk aqueous phase to the metal surface is, therefore, important. Since water is the medium which carry these species, it is assumed here that the amount of water molecules which is present in the vicinity of the metal surface is a good measure of corrosion. For these reasons, the water molecules are counted which are present across the entire thickness of the surfactant molecules, and not only the ones which are present at the metal surface (z < 5 Å). In terms of least amount of water present within the adsorption morphologies, decanethiol molecules are the most effective, the quat-12 + pe-12 mixture comes next, followed by quat-12, quat-12 + quat-4 / quat-4. This result is in agreement with prior electrochemical observations in which decanethiol molecules

showed better corrosion inhibition efficiency in comparison to the quat molecules [93,



Figure 3.8. Density profile of water as a function of distance, *z* from the metal surface in the absence and presence of adsorbed surfactants. Water is completely excluded from the metal surface in the case of decanethiol adsorption, whereas layers of water close at the metal surface are observed in other systems. The density of water is 1 g/cc. The peaks in the density of water beyond 1 g/cc is a mathematical artifact which occurs because of obtaining the density of water in small bins of widths 0.15 Å, which is smaller than the size of a water-oxygen ($d \sim 3.166$ Å).

94].

3.5 Conclusions

In this work, a new umbrella sampling-based methodology is introduced that enables the study of equilibrium adsorbed morphologies of surfactant molecules at interfaces. Using this methodology, the equilibrium adsorbed morphologies of cationic surfactants of different alkyl tail lengths (quat-12 and quat-4), an uncharged surfactant (decanethiol), a mixture of cationic and anionic surfactants (quat-12 and pe-12), and a mixture of quat-12 and quat-4 surfactants are compared. The results show that cationic surfactants with small alkyl tail lengths (quat-4) attain only partial coverage of the surface with the molecules lying parallel to the surface. The cationic molecules with longer tail lengths (quat-12) adsorb as micelles sitting on top of a monolayer of molecules lying parallel to the surface. In contrast to the cationic surfactants, charge-neutral decanethiol adsorbs as a self-assembled bilayer with the molecules standing up in the first layer and densely packing the surface. Mixtures of cationic and anionic surfactants show a synergistic improvement in the adsorption behavior. Overall, it is concluded that the accumulation of charge limits adsorption, whereas lateral hydrophobic interactions between the alkyl tails favor adsorption. The proposed simulation methodology can be employed to study many different surfactant systems and will help in providing a rational understanding of the rich adsorption behavior of surfactants on metallic, polar, and hydrophobic surfaces.

Chapter 4: Hydration of Linear Alkanes is Governed by the Small Length-Scale Hydrophobic Effect^[*]

4.1 Introduction

Hydrophobic interactions in water are ubiquitous in driving various nanoscale processes, including protein folding [99], ligand binding [100], formation of biological membranes [101], and surfactant micelles [44, 66], and self-assembly of surfactants at metal-water interfaces [18]. These processes are strongly influenced by the size and shape of hydrophobic solutes. For instance, surfactants with longer alkyl tails (> 6)manifest better micellization tendency in the aqueous phase, and stronger adsorption tendency at the metal-water interface as compared to the ones with smaller tails [81, 93]. Concave-shaped surfaces are argued to be more hydrophobic than the flat or convexshaped ones [102]. Hydration thermodynamics is understood to be length-scale dependent. Hydration of small spherical solutes ($d \lesssim 0.8$ nm) is entropically-driven, accompanied by the formation of a hydrogen-bonded network of water molecules around the solute, which results in loss of configurational freedom [103]. The hydration free energy of small hydrophobic solutes is characterized by the nature of density fluctuations in the volume of bulk water equivalent to the volume occupied by the solute [104]. Above a critical size of a spherical solute ($d \ge 2$ nm), water molecules can no longer retain their hydrogen-bonded network around the solute. This causes surface dewetting, and an enthalpy penalty [103]. Hydration of large spherical solutes is, thus, driven by this enthalpy loss [105]. Upon dewetting, the solute-water interface becomes akin to an airwater interface and, therefore, the hydration free energy of large solutes is well-captured by the air-water interfacial energy [106].

Enthalpic-entropic contributions to hydration free energy are well-understood for spherical solutes. However, such an understanding is lacking for anisotropic solutes, such as linear alkanes. Whether it be protein folding, adsorption of surfactants, or contamination of water with oil [107-109], the underlying phenomenon playing a critical role is the hydrophobic interactions of hydrocarbon chains. Therefore, deciphering the hydration behavior of linear alkanes is key to understanding these varied processes [110].

Hydration of linear alkanes has been previously studied using both molecular simulations and experiments. Hydration free energies of linear alkanes, up to hexane and decane, have been estimated via free energy perturbation (FEP) [111] and scaled particle theory (SPT) [112], respectively. Ferguson, *et al.*, employed incremental Widom insertion method in replica exchange molecular dynamics (MD) simulations to study hydration of large linear alkanes up to docosane, but did not decouple the energetic and entropic contributions [110]. Other works have focused on only a few alkanes [107]. In experiments, hydration free energies and enthalpies of alkanes ranging from methane to octane have been determined [113, 114]. Because of low solubilities, experimental determination of the hydration free energy of longer alkanes is unreliable [110]. Along with their hydration, aggregation of alkanes at air-water interfaces has been studied in both experiments [115] and simulations [116] because of its importance in understanding detergency [117], behavior of amphiphilic polymers [118] and proteins at aqueous interfaces [119]. In this work, umbrella sampling in MD simulations is used to determine the free energy profiles of alkanes, ranging from methane (henceforth referred to as C-1) to octadecane (henceforth referred to as C-18), across the air-water interface [41]. It is a simple yet powerful approach that provides the hydration free energies as well as the free energies of adsorption at the air-water interface. The hydration enthalpies and entropies, obtained from these simulations, help in understanding the nature of hydration thermodynamics of linear alkanes. The results reveal that the hydration of linear alkanes, in the range of C-1 to C-18, is governed by the small length-scale hydrophobic effect. The unfavorable hydration free energy is dominated by the loss of entropy. There is a favorable enthalpic change, but it is smaller than the entropic contribution. The interfacial energy associated with the formation of a cavity during the hydration of alkanes does not explain the hydration free energies, confirming that the studied alkanes follow the small length-scale hydrophobic effect.

4.2 Simulation System and Methods

All-atom MD simulations of linear alkanes in infinite dilution are performed near an air-water interface. The simulation system is shown in Figure 4.1. The simulation box is periodic in the *x*- and *y*- directions (parallel to the air-water interface). The *z*-direction is non-periodic and is bound by two surfaces. The bottom surface at z = 0 is kept slightly attractive to the water molecules to prevent any vertical displacement of the water column [refer to Equation (S1), Supporting Information (Appendix C) for the interaction parameters]. The top surface in *z*-direction of the simulation box is an athermal surface, to restrict the molecules within the simulation box. The size of the simulation box for studying C-1 to C-6 molecules is 20 Å × 20 Å × 60 Å, whereas the size for studying C-8 to C-18 molecules is 52.61 Å \times 52.61 Å \times 80 Å. A larger size of the simulation box for longer alkanes is needed to ensure that the alkanes do not interact with their periodic images. A vacuum space of height ~ 30 Å is kept above the water column for calculating the free energies of alkanes in vacuum. The number of water molecules in the two simulation boxes are 415 and 4380 respectively. The interaction potential parameters of alkanes are obtained from General Amber Force Field (GAFF) [29], and the water molecules are represented by the Simple Point Charge Enhanced (SPC/E) model [90]. Partial charges on the alkane atoms are calculated in implicit aqueous medium from density functional theory (DFT) by employing B3LYP hybrid functional with 6-31G (d, p) basis set. The DFT calculations are performed using Gaussian 16 [89]. The MD simulations are performed in isochoric-isothermal ensemble (constant number of particles N, volume V, and temperature T) at T=300 K. The vacuum space above the water column ensures that the system pressure is maintained at the saturation pressure corresponding to T=300 K [70]. The vacuum space is therefore a vapor phase but, for simplicity, it is referred to as air for the rest of the discussion. Alkanes when present in air undergo Brownian dynamics motion [120]. Therefore, Langevin dynamics is performed on the alkanes when they are in air. Based on the prior experimental and simulation works, the damping coefficient for the Langevin dynamics in air is taken as 0.00125/ps for each atom of the alkanes [121, 122]. The cutoff distance for Lennard-Jones (LJ) and shortrange Coulombic potential is chosen as 10 Å. Long-range Columbic interactions are computed using the particle - particle - mesh (pppm) method. All MD

simulations are performed using large-scale atomic/molecular massively parallel simulator (LAMMPS) [71].



Figure 4.1: Simulation snapshots of C-10 (a) in air, (b) at the air-water interface, and (c) in water. The red beads represent carbon atoms of the molecule, and the cyan dots represent water molecules.

Free energy calculations of hydration of alkanes are performed via umbrella sampling as follows. An external biased harmonic potential, U is applied on the center-of-mass of an alkane along the z-direction as:

$$U(\xi,\xi_0) = \frac{1}{2}k(\xi-\xi_0)^2 \tag{4.1}$$

where k is the force constant (= 5 kcal/mol/Å²) and ξ is the z coordinate of the center-ofmass of the alkane from the air-water interface. The air-water interface ($\xi = 0$ Å) is the location where the density of water is 0.5 g/cc [refer to Figure S1, Supporting Information (Appendix C)]. ξ_0 is the set value of the z coordinate for an umbrella sampling window. The implementation is done using the COLVARS package in LAMMPS [88]. The umbrella sampling windows are generated by changing ξ_0 in increments of 0.5 Å to ensure sufficient sampling along the z axis. The umbrella sampling windows are combined to generate the free energy profiles using weighted histogram analysis method (WHAM) [87]. Each umbrella sampling window is run for 20 ns for equilibration followed by another 20 ns for production.

4.3 Results and Discussion

Figure 4.2 (a) shows the free energy profiles of alkanes across the air-water interface. The free energy is minimum at $\xi \approx 2$ Å for all the alkanes. As expected, it is unfavorable for the alkanes to be in water. C-18, the longest alkane studied by us, has the most and C-1 has the least favorable free energy to enter water from the interface. The hydration free energy, ΔF_{hyd} is the difference in the free energies in bulk water and in air. Figure 4.2 (b) shows that the calculated hydration free energy varies linearly with the alkane length. Also shown in this figure is the comparison of the hydration free energy estimates with the previous estimates from SPT, FEP, and Widom insertion method. other estimates. The hydration free energy values of this work fall in between the values calculated from the SPT and FEP methods, and the three estimates are quite close up to C-6 [111, 112]. Beyond C-6, the values obtained from SPT diverges away from this work. The free energy estimates from the Widom insertion method are much lower than this work.



Figure 4.2: (a) Free energy profiles of alkanes as a function of the distance of their center-of-mass, ξ from the air-water interface. The vertical dotted line demarcates the air-water interface ($\xi = 0$ Å). The hydration free energy, ΔF_{hyd} for C-18 is marked by an arrow. The error bars are determined by generating three independent free energy profiles for each alkane. (b) Comparison of the hydration free energies with SPT, FEP and Widom insertion methods [110-112]. The size of error bars of the hydration free energy estimates is smaller than the size of the markers.

The ΔF_{hyd} can be broken down into two components: the free energy of forming a cavity of the size of the solute in water, ΔF_c , plus the solute-water interaction energy [111, 112]. Figure 4.3(a) shows the solute-water interaction energies of the alkanes as a function of ξ obtained in the simulations. across the air-water interface [see Figure 4.3 (a)]. Since the alkanes are non-polar molecules, the only interaction they have with water is the LJ interaction. C-18 has the most favorable LJ interaction with water while C-1 has the least. The free energy of cavity formation, ΔF_c can be computed using:

$$\Delta F_c = \Delta F_{hyd} - \Delta L J_{hyd} \tag{4.2}$$

Figure 4.3 (b) shows the values of ΔF_c for all the alkanes. Interestingly, it is found an excellent match with the values predicted from the SPT and FEP methods [111, 112]. In the SPT and FEP methods, the cavity formation free energies and the alkane-water interaction energies are independently calculated, and then they are summed up to give the hydration free energies.



Figure 4.3: (a) Alkane-water LJ interaction energy of alkanes as a function of the distance of center-of-mass of alkanes, ξ from the air-water interface. The LJ interaction energies are minimum when the alkanes are fully solvated in water. The arrow shows the change in alkane-water interaction energy upon hydration, ΔLJ_{hyd} for C-18. (b) Comparison of the cavity formation free energies, ΔF_c of this work with the SPT and FEP estimates [111, 112]. The size of error bars of the cavitation free energy estimates are smaller than the size of the markers.

The enthalpic and entropic contributions to the hydration free energy of alkanes are computed. Because $P\Delta V \approx 0$, the enthalpy of hydration, $\Delta H_{hyd} \approx \Delta U_{hyd}$, where ΔU_{hyd} is the change in the total internal energy of the system upon hydration. Figure 4.4 (a) shows the total internal energy, ΔU as a function of ξ for the alkanes. For the ease of visualization, the profiles have been shifted so that the minimum is set to 0. The ΔU profiles have the minima at $\xi \approx -2$ Å, unlike the free energy profiles where the minima is at $\xi \approx 2$ Å. The $\Delta U_{hyd} < 0$ for all the alkanes, which means that the hydration of linear alkanes is enthalpically favorable. Correspondingly, the entropy of hydration, $T\Delta S_{hyd}$ of the alkanes can be deduced using:

$$T\Delta S_{hyd} = \Delta U_{hyd} - \Delta F_{hyd} \tag{4.3}$$

The $T\Delta S_{hyd}$ of the alkanes is shown in Figure 4.4 (b). $T\Delta S_{hyd} < 0$ indicates that the hydration of all the alkanes, including the ~2.4 nm long C-18, is entropically unfavorable. Moreover, the $T\Delta S_{hyd}$ values decrease linearly with the alkane length, suggesting that the nature of $T\Delta S_{hyd}$ is not expected to change unless the alkanes become large enough that they attain folded conformations in water. This finding implies that the hydration behavior of linear alkanes is governed by the small length-scale hydrophobic effect and differs from that of large spherical and extended planar hydrophobic solutes, for which the hydration free energy is entropically favorable [103, 106, 123, 124]. The hydration of linear alkanes is understood as follows. Because of the anisotropic shape of linear alkanes, neighboring water molecules are able to retain their hydrogen bonds around the methyl groups. The hydration entropy is, indeed, experimentally determined to be unfavorable for alkanes up to octane ($l \approx 1$ nm) [113, 114]. Low solubilities of longer alkanes pose experimental challenges in accurately determining their hydration behavior [110].



Figure 4.4: (a) Total internal energy, ΔU of the system as a function of the distance of center-of-mass of alkanes, ξ from the air-water interface. The profiles show ensemble-average energies at each location. The total internal energy of the small (C-1 to C-6) and the large systems (C-8 to C-18) are of the order of ~-7500 k_BT and ~-80000 k_BT respectively. Therefore, the energy profiles of all the systems are shifted to zero for ease of representation and for reading only the change in the energy, ΔU . The presence of large fluctuations in the profiles of big systems is a result of their large internal energies. Error estimates in the energies are calculated from block averages. ΔU_{hyd} is obtained as the difference between ensemble-average energies at all positions in the bulk water and bulk air. The arrow indicates ΔU_{hyd} for C-18. (b) Estimation of $T\Delta S_{hyd}$ from ΔF_{hyd} and ΔU_{hyd} . A linear dependence of ΔU_{hyd} and $T\Delta S_{hyd}$ on the alkane length is observed.

The ΔU_{hyd} can be written as:

$$\Delta U_{hyd} = \Delta U_{hyd}^{water-water} + \Delta U_{hyd}^{intramolecular} + \Delta LJ_{hyd}$$
(4.4)

where $\Delta U_{hyd}^{water-water}$ and $\Delta U_{hyd}^{intramolecular}$ are the changes in the energetics of waterwater interactions and the intramolecular interactions of the alkane molecule, respectively upon hydration of the alkane. While $\Delta U^{water-water}$ includes both LJ and Coulombic contributions, $\Delta U^{intramolecular}$ comprises of bonded, angular, dihedral, as well as LJ + coulombic interactions. Figure S2 [Supporting Information, Appendix C] shows $\Delta U^{intramolecular}$ as a function of the distance of the alkane from the air-water interface. It is found that the $\Delta U_{hyd}^{alkane} \approx 0$. Therefore, equation (4.4) is simplified to:

$$\Delta U_{hyd} = \Delta U_{hyd}^{water} + \Delta L J_{hyd} \tag{4.5}$$

By comparing the figures 4.3 (a) and 4.4 (a, b), it is noted that $\Delta U_{hyd}^{water} > 0$. This implies that water-water interactions are also disrupted upon the hydration of linear alkanes. Although this is intuitive for hydration of large-scale solutes wherein water loses hydrogen bonds [103], the loss on water-water interactions for the small sized solutes is also noted here. Even the hydration of the smallest solute (C-1) causes the energy of water to drop by ~4.3 *k*_B*T*. However, the favorable change in ΔLJ_{hyd} is dominant in all cases, making the overall enthalpic change negative.

The change in entropy of the system upon hydration, ΔS_{hyd} can be written as: $\Delta S_{hyd} = \Delta S_{hyd}^{water} + \Delta S_{hyd}^{alkane}$ (4.6)

where ΔS_{hyd}^{water} and ΔS_{hyd}^{alkane} are the entropic changes of water and alkane molecules, respectively. As it is shown, $\Delta U_{hyd}^{intramolecular} \approx 0$ [Figure S2, Supporting Information, Appendix C], which is also supported by the conformational-biased MD simulations performed by Ferguson, *et al.*, [110] in which it is observed that linear alkanes up to C-18 do not collapse or undergo a conformational change upon hydration. As expected, in both air and water, the alkane molecules in infinite dilution retain all their orientational and translational freedom [Figure S3 (Supporting Information, Appendix C)]. Therefore, $\Delta S_{hyd}^{alkane} \approx 0$. Equation (4.6) is simplified as:

$$\Delta S_{hyd} = \Delta S_{hyd}^{water} \tag{4.7}$$

Equation (4.7) suggests that the negative hydration entropy [Figure 4.4 (b)] is a result of entropic loss of water molecules due to the formation of hydrogen bonds around the alkane.

The large length-scale hydration thermodynamics follows $\Delta F_{hyd} = \gamma \Delta A_{hyd}$, where γ is the surface tension at the air-water interface and ΔA_{hyd} is the interfacial area created by the solute in water [103, 106, 125]. On the other hand, the hydration free energy of small sized solutes does not follow $\gamma \Delta A_{hyd}$, but is associated with water density fluctuations based on gaussian statistics in the volume of bulk water equivalent to the volume of the solute [104, 126]. The interfacial energy, $\gamma \Delta A_{hyd}$ is calculated to determine if it is related to the hydration free energy of the alkanes that are studied. The interfaces are obtained by identifying the instantaneous interfaces proposed by Willard, *et al.*, [127]. Figure 4.5 (a) shows a snapshot of the air-water and alkane-water interfaces for the case of C-6 located at $\xi = -10$ Å. The interfacial area, ΔA_{hyd} , is determined by first triangulating the interfaces using *isosurface* function in MATLAB, and then summing up the areas of all the triangles. Figure 4.5 (b) shows the change in interfacial energy as the alkanes go from air to water. As expected, C-18 has the largest interfacial energy among the studied alkanes.



Figure 4.5: (a) Snapshot of a system showing air-water and alkane-water interfaces in presence of C-6 at $\xi \approx -10$ Å. The interfaces are shown in red. (b) Interfacial energy profiles as a function of the distance of center-of-mass of alkanes, ξ from the air-water interface. $\gamma = 63.6$ mJ/m² for SPC/E water model.[128] The profiles show ensembleaverage interfacial energies at each location. The minimum of all the profiles is shifted to zero. The arrow indicates the change in interfacial energy upon hydration of C-18. A bulge in the profiles (prominently for smaller alkanes – C-1 to C-8) is observed. The explanation of this behavior is given in Figure S5 [Supporting Information, Appendix C].

The interfacial energy, $\gamma \Delta A_{hyd}$, obtained above is compared to the free energy of hydration, ΔF_{hyd} , and the free energy of cavity formation, ΔF_c , in Figure 4.6. Clearly,

 $\Delta F_{hyd} \neq \gamma \Delta A_{hyd} \neq \Delta F_c$, except for C-5 and C-6, where there is a cross-over of ΔF_{hyd} and $\gamma \Delta A_{hyd}$. This strengthens the assertion that the hydration of linear alkanes is not governed by the alkane-water interfacial energy. Figure S4 [Supporting Information, Appendix C] compares $\gamma \Delta A$ profiles with ΔF profiles for each of the individual alkanes.



Figure 4.6: Comparison of $\gamma \Delta A_{hyd}$ with ΔF_{hyd} and ΔF_c for all the alkanes. The size of the error bars is smaller than the size of the markers.

4.4 Conclusions

In this work, the length-scale dependence of hydration thermodynamics of linear alkanes ranging from methane to octadecane is studied. From the calculations of free energy, enthalpy, and entropy of hydration, it is found that the hydration of all the studied alkanes is entropically driven, and thus governed by the small length-scale hydrophobic effect. This result contrasts with the hydration of spherical solutes where the hydrophobic effect changes from entropically- to enthalpically-driven as the size of the solutes increase. The assertion is bolstered by showing that the hydration free energies of alkanes do not match free energetic cost of creating an air-water like interface in the hydrated state. The findings on linear alkanes show that hydration of hydrophobic solutes is not just characterized by their size, but also their shape. The free energy calculations also reveal the affinity of linear alkanes to adsorb onto the air-water interface.

Chapter 5: Understanding the Hydration Thermodynamics to Enhance Aqueous Solubility and Reduce Micellization Tendency of Surfactant Molecules^[**] 5.1 Introduction

One important characteristic of the surfactant molecules in all these applications is their aqueous solubility. A good aqueous solubility ensures that surfactant molecules have sufficient concentration in the aqueous medium to aggregate at the solid- or oilwater interfaces. Poorly soluble surfactants phase separate out of the aqueous medium [129, 130]. For instance, surfactant molecules that are added to oil pipelines for the mitigation of internal corrosion should have sufficient aqueous solubility to adsorb on to the metal-water interface, rather than aggregating at the oil-water and gas-water interfaces, which would render them ineffective [28, 131-138]. Therefore, improving the aqueous solubility of surfactants is a worthwhile pursuit for many applications. Conditions such as increased salinity, and low pH have been shown to enhance aqueous solubility of cationic surfactants [28, 136, 138]. Ionic surfactants have higher aqueous solubility as compared to the non-ionic surfactants with the same alkyl tail because of the strong tendency of ions to be solvated in water. In addition to their low solubility, the aggregation of long alkyl tail surfactants into micelles is another concern as the surfactants in micellar form may not adsorb at the metal-water interfaces. It is previously reported that cationic surfactant micelles experience a long-range free energy barrier to adsorption at the metal-water interface [66, 73].

Zahariev, *et al.*, determined free energies of pentanol, hexanol, and heptanol molecules across oil-water interfaces and found them to prefer the oil phase [139]. Other

computational and experimental studies have investigated the effect of the alkyl tail length on the hydration free energies and have reported the hydration free energy to linearly increase with the addition of each methylene group [107, 110-114, 140]. On the other hand, the hydration free energy decreases with the size of the polar head groups [107]. Nonionic surfactants, though less water-soluble, may serve as better corrosion inhibitors in some applications because of their tendency to adsorb at the metal-water interfaces in high-density adsorbed morphologies. For example, decanethiol adsorbs at metal-water interfaces much better than the cationic alkyl dimethyl benzyl ammonium bromide molecules [93, 94]. Computational and experimental works reveal that hydrophobic interactions between long alkyl tails of surfactant molecules facilitate adsorption at metal-water interfaces in high-density morphologies [18, 81]. Thus, the interfacial adsorption characteristics and aqueous solubility of surfactants often evolve orthogonally in molecular design.

In this work, the hydration free energy of cationic quaternary ammonium chloride and charge-neutral amine surfactants of different alkyl tail lengths are determined. The enthalpic and the entropic contributions of the alkyl tail and the polar head group are decoupled. Furthermore, it is shown that by making the alkyl tail polar via replacement of the terminal methyl group with a hydroxyl group increases the aqueous solubility of the surfactants by ~100 times. Addition of the hydroxyl group to the alkyl tail also decreases the micellization tendency of the surfactant molecules. These results demonstrate that the solubility and aggregation characteristics of long alkyl tail surfactants can be tuned by simple point substitutions.

5.2 Simulation System and Methods

Figure 5.1 (a, b, c, d) shows the surfactant and the alkane molecules that are studied using molecular dynamics simulations. The molecules are cationic quaternary ammonium-based surfactant molecules (henceforth referred to as quat-n) [Figure 5.1(a)], uncharged amine-based surfactant molecules (henceforth referred to as amine-n) [Figure 5.1(b)], cationic quaternary ammonium-based surfactant molecules with a terminal hydroxyl group (henceforth referred to as quat-n-OH) [Figure 5.1(c)], and linear alkane molecules (henceforth referred to as C-n) [Figure 5.1(d)], where n denotes the length of the alkyl tail of the molecules. Quat and amine molecules are chosen because they are widely used for corrosion inhibition of oil-and-gas pipelines [13, 141]. The MD simulations are performed in a two-phase system comprising of liquid water and its vapor phase. A snapshot of the simulation system with a quat-10 molecule in the liquid phase is shown in Figure 5.1 (e).



Figure 5.1. Structure of the (a) quat-*n* molecules (n = 9/15 for quat-10/quat-16), (b) amine-*n* molecule (n = 9 for amine-10), (c) quat-*n*-OH molecules (n = 9/15 for quat-10-OH/quat-16-OH), (d) C-*n* molecules (n = 9/15 for C-10/C-16). (e) A snapshot of the simulation system with a quat-10 molecule in the aqueous medium. The red beads represent the polar head group of the molecule, the yellow beads represent the hydrophobic alkyl tail, the blue bead represents the chloride counter-ion, and the small cyan dots represent the water oxygens.

The size of the simulation box is 52.61 Å × 52.61 Å × 85 Å. The simulation box is periodic in *x*- and *y*- directions, but non-periodic in the *z*- direction. The nonperiodicity is maintained by the two walls placed at z = 0 and z = L, where L is the length of the simulation box in the *z*- direction. The wall at z = 0 has an attractive interaction with the water molecules so that the water bath stays at the bottom section of the simulation box. The attractive interaction potential between the bottom wall and the water molecules is given in Equation S1 [Supporting Information, Appendix D]. The bottom wall is made reflective to all other species of the system. The wall at z = L is athermal and is made reflective to all the atoms of the simulation system. The interaction potential parameters of the surfactant and alkane molecules are obtained from general amber forcefield (GAFF) [29]. The partial charges on the surfactant atoms are computed from density functional theory (DFT) by employing B3LYP hybrid functional with 6-31G (d, p) basis set. The DFT calculation is performed in implicit water using Gaussian 16 [89]. The extended simple point charge model (SPC/E) is employed for the water molecules [90]. Since the quat molecules are cationic with a charge of +1, a chloride ion is introduced as a counter-ion to maintain charge neutrality of the simulation box. The potential parameters of the chloride ion are taken from the Joung-and-Cheatham's model [68]. The simulations are performed in the isothermal-isochoric ensemble at T = 300 K, wherein the number of species (N), volume of the system (V), and temperature of the system (T) are held fixed. The presence of a vacuum space adjacent to the water phase ensures that the system pressure is maintained at the saturation pressure corresponding to the fixed temperature [70]. The vacuum space is therefore a vapor phase, but for simplicity, it is henceforth be referred as the air phase. Like in the liquid water, the surfactant molecules also experience Brownian-dynamics motion while in the air [120]. Therefore, Langevin dynamics is performed on the molecules when they are present in the air. The damping coefficient for the Langevin dynamics is taken as 0.00125/ps for each atom of the molecules based on the prior experimental and simulation works [121, 122]. The cutoff distance for Lennard-Jones and short-range Coulombic potentials is taken as 10 Å. The long-range Coulombic potential is computed using the particleparticle-particle-mesh (pppm) method. The number of water molecules in the system is 4382. The surfactant and the alkane molecules are simulated in infinite dilution, using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [71].

Free energy profiles of the molecules across the air-water interface are generated using the umbrella sampling technique [41]. The air-water interface is the location where the average density of the water molecules is 0.5 g/cc [refer to Figure S1, Supporting Information (Appendix D)]. This position is marked as $\xi = 0$ Å. In umbrella sampling technique, a biased potential is applied to the center-of-mass of the molecules using a harmonic potential as:

$$U(\xi,\xi_0) = \frac{1}{2}k(\xi - \xi_0)^2$$
(5.1)

where k is the force constant, ξ_0 is the set position of the molecule from the air-water interface, and ξ is the instantaneous position of the molecule at any time. The Colvars implementation in LAMMPS is used to apply biased potential to the molecules [88]. The biased potential at a set position restricts the molecule to sample a bin of some width which depends on the stiffness of the harmonic potential, *k*. In this work, k = $5 \ kcal/mol$ and the sampling positions are set at an interval of 0.5 Å. It is found that this interval is sufficiently small to obtain overlapping histograms of the sampling distributions. The weighted histogram analysis method (WHAM) is then invoked which combines all the biased simulations and produces the free energy profile based on the unbiased probabilities [87]. All the simulations are first run for 20 ns to let the system reach equilibrium, and then run for the next 20 ns for use in calculation of thermodynamic properties. All the free energy profiles are generated by three independent simulations.

The simulation system for performing unbiased isobaric-isothermal simulations of quat-10-OH molecules in the bulk aqueous phase and for performing biased umbrella sampling simulations of an amine micelle across air-water interface is discussed later in the text.

5.3 Results and Discussion

5.3.1 Free Energy and Enthalpy Profiles of Quat and Alkane Molecules

Free energy profiles of the two cationic quat molecules (quat-10 and quat-16) and two alkanes (C-10 and C-16) across air-water interface is calculated and shown in Figures 5.2 (a, b). The free energy of the molecules is minimum at the interface, indicating that the interface is the most preferred location for the molecules. Since the alkanes are hydrophobic molecules, they show an unfavorable free energy to go from bulk air to bulk water. The quat molecules, on the other hand, show a favorable free energy of hydration. The free energy of the quat molecules is significantly high in the bulk air than in the bulk water. This supports the prior experimental work which reported that in a two phase water-oil system, the quat molecules stay in the water phase and do not enter the oil phase [135]. A significant difference of $6 k_B T$ is observed between the free energies of the quat molecules and alkanes in water. This suggests that the quat head group has an appreciable contribution of 6 k_BT towards lowering the free energy barrier for a molecule to go from the interface to the bulk water. Another interesting observation is that the free energies of quat-16 and C-10 in water are the same, which is 14 k_BT. Since quat-16 has six more methylene groups in its hydrocarbon tail than C-10, this implies that the quat head group negates the unfavorable free energy contribution coming from a linear tail of six methylene groups (C-6). Also, the free energy barrier for quat-16 to go from the interface to the bulk aqueous phase is $6 k_B T$ larger than it is for quat-10. The increased energetic barrier for quat-16 is associated with its longer hydrophobic length. A

one-to-one comparison of the free energy profiles of quat-10 and quat-16 molecules is shown in Figure S2 [Supporting Information, Appendix D].



Figure 5.2. Free energy profiles of (a) quat-10 and C-10, (b) quat-16 and C-16 molecules with respect to the distance of their center-of-mass from the air-water interface, ξ . The air-water interface is located at $\xi = 0$ Å, and is marked by a vertical dotted line. The free energy profiles are shown up to 30 k_BT, however the free energy profiles of quat molecules go beyond 50 k_BT in the air. The size of the error bars of the free energy profiles are smaller than the size of the markers.

A sharp increase in the free energy profiles of quat molecules in the form of a convex function is noted when going from the interface to the bulk air, i.e., $\Delta F''(\xi) > 0 \forall \xi > 0$ Å. Such a long-range convexity is not observed in case of the alkanes. The reason is that, even when the quat molecules are placed up in the air, their polar head

groups point downwards to remain solvated with the water molecules. As a result, the interfacial water molecules get pulled upwards, thereby increasing the interfacial area of the air-water interface [also refer to Figures S3 (a, b), Supporting Information (Appendix D)]. This leads to an increase in the air-water interfacial energy, which is captured in these free energy profiles beyond $\xi = 0$ Å.

The free energies of the alkanes are minimum at $\xi = 2$ Å, where they lie parallel to the air-water interface. The free energies of quat-10 and quat-16 molecules are, however, minimum at $\xi = -1$ Å and $\xi = 0$ Å. At these locations, the quat molecules are oriented in such a way that their polar head groups are submerged in the water, and their hydrophobic tails protrude outside the water [refer to Figures S3 (c, d), Supporting Information (Appendix D)]. The spatial and orientational distributions of the alkane and the quat molecules at their respective free energy minima locations are shown in Figures S4 (a, b), S5 (a, b) and S6 [Supporting Information (Appendix D)].

The enthalpy profiles are computed using the relation:

$$\Delta H = \Delta U + P \Delta V \tag{5.2}$$

where ΔU is the total internal energy of the system. Since $P\Delta V \approx 0$, $\Delta H \approx \Delta U$. Figure 5.3(a) shows the ΔU profiles for the quat molecules. From the ΔU profiles, the enthalpy change for the quat molecules to go from the interface to the bulk aqueous phase, $\Delta U_{i/w}$, is obtained where the subscript i/w represents interface/water. It is found that for both the molecules, $\Delta U_{i/w} > 0$. It is, indeed, expected that the transfer of hydrophobic tails into water breaks some hydrogen bonds between water molecules, leading to an unfavorable change in the total internal energy.



Figure 5.3. (a) Enthalpy profiles of quat molecules with respect to the distance of their center-of-mass from the air-water interface, ξ . The change in enthalpy for the quat-16 molecule to go from its free energy minimum location, $\xi = 0$ Å to the bulk water is indicated by an arrow. (b) Enthalpic-entropic contributions to the free energy for quat molecules.

The entropy change, $T\Delta S_{i/w}$ is calculated using the relation:

$$T\Delta S_{i/w} = \Delta H_{i/w} - \Delta F_{i/w} \tag{5.3}$$

and is shown pictorially in Figure 5.3 (b). It is found that $T\Delta S_{i/w} < 0$ and $T\Delta S_{i/w}^{quat-16} < T\Delta S_{i/w}^{quat-10}$. The entropy loss can be broken down into two components as:

$$T\Delta S_{i/w} = T\Delta S_{i/w}^{quat} + T\Delta S_{i/w}^{water}$$
(5.4)

where $T\Delta S_{i/w}^{quat}$ and $T\Delta S_{i/w}^{water}$ are the entropic contributions coming from the quat molecule and the water molecules, respectively. Figures S5 (a, b) [Supporting

Information, Appendix D] compare rotational distributions of quat molecules at the airwater interface with their distributions in the bulk water. The distributions show that the quat molecules have more rotational degrees of freedom in the water than at the interface, i.e., $T\Delta S_{i/w}^{quat} > 0$. The equation (5.4) therefore suggests that although $T\Delta S_{i/w}^{quat} > 0$, the water molecules lose enough entropy that the overall entropy of transfer of quat molecules into the water is negative. It is also determined in a prior work that the entropic loss of water molecules is attributed to the formation of hydrogen-bonded cages of water molecules around the linear hydrocarbon tails [140]. The hydrogen bonded cages around the hydrocarbon chains restrict the conformational degrees of freedom of the water molecules, thereby decreasing their entropy.

5.3.2 Free Energy and Enthalpy Profiles of Amine Molecule

The free energy of the uncharged amine-10 molecule, along with the C-10 molecule is shown in Figure 5.4 (a). The free energy profiles of both the molecules overlap in the range between the interface and the bulk water ($\xi \leq 2$ Å). This indicates that both the molecules have the same tendency to move between the interface and the bulk water. The amine head group, therefore, does not show any additional contribution in the free energy of transfer from the interface to the water. It is, however, important to mention that the free energy of hydration of the amine-10 molecule is different from that of the C-10 molecule. The free energy of hydration of a molecule is given by the difference between its free energies in bulk water and bulk air, $\Delta F_{a/w}$, where the subscript a/w corresponds to air/water. From Figure 5.4 (a), it is noted that the $\Delta F_{a/w}$ of the amine-10 molecule is 7.5 k_BT, whereas that of the C-10 molecule is 10.5 k_BT.

Therefore, although the amine-10 molecule shows a better hydration tendency than the C-10 molecule, it still has an unfavorable free energy to go from the bulk air to the bulk water. McMohan has observed the similar behavior experimentally, wherein the uncharged imidazoline surfactant molecule showed a high solubility in the oil phase, but minimal affinity for the water phase.[137] The behavior of uncharged surfactant molecules contrasts with the behavior of the charged quat molecules which show a much favorable free energy to go from the bulk air to the bulk water (see Figure 5.2).



Figure 5.4. (a) Free energy profiles of the amine-10 and C-10 molecules with respect to the distance of their center-of-mass from the air-water interface, ξ . The free energy of hydration, $\Delta F_{a/w}$ for the amine-10 molecule is indicated by an arrow. The size of the error bars of the free energy profiles are smaller than the size of the markers. (b) Enthalpy profiles of the amine-10 and C-10 molecules with respect to the distance of their center-

of-mass from the air-water interface, ξ . The enthalpy of hydration, $\Delta U_{a/w}$ for the amine-10 molecule is indicated by an arrow.

A comparison of the free energy profiles of the amine-10 molecule with the quat molecules is shown in Figure S7 [Supporting Information, Appendix D]. The free energy profile of amine-10 molecule is not a long-range convex function beyond $\xi > 0$ Å as in the case of quat molecules. This is because the amine-10 molecule is uncharged, and therefore does not pull water molecules towards itself when present in the air [refer to Figure S8 (a), Supporting Information, Appendix D]. The amine-10 and C-10 molecules have the free energy minimum at $\xi = 2$ Å. At $\xi = 2$ Å, while the C-10 molecule lies on the air-side and parallel to the interface, the amine-10 molecule is inclined in such a way that its polar head group lies inside the water, and its hydrophobic tail protrudes out of the water [refer to Figure S8 (b), Supporting Information (Appendix D)]. The spatial and orientational distributions of the amine-10 molecule at the free energy minimum location are shown in Figures S9 (a, b) [Supporting Information (Appendix D)].

The enthalpy profiles, ΔU of the amine-10 and C-10 molecules are shown in Figure 5.4 (b). The enthalpy of hydration, $\Delta U_{a/w}$ of both the molecules is negative, with $\Delta U_{a/w}^{amine-10} < \Delta U_{a/w}^{C-10}$. The entropy of hydration, $T\Delta S_{a/w}$ is obtained for the molecules and is shown pictorially in Figure S10 [Supporting Information, Appendix D]. Also shown are the values for C-11 (undecane) predicted from the previous work [140]. The only difference in the amine-10 and C-11 molecule is the presence of a different heavy terminal atom – nitrogen in amine-10 and carbon in C-11. It is found that $T\Delta S_{a/w}^{amine-10} <$ $T\Delta S_{a/w}^{C-11}$. Since the only difference between the amine-10 and C-11 molecule is the presence of nitrogen atom in place of the carbon atom, it can be postulated that the large entropic loss to the water molecules around the amine molecule is attributed to the strong layering of water molecules around the polar nitrogen atom.

5.3.3 Free Energy Profiles of Quat-OH Molecules

The free energy profiles of surfactant molecules and alkanes, discussed above, show that the polar atoms such as nitrogen, play an important role in providing enhanced aqueous solubility to the surfactant molecules. A hydroxyl group (-OH) is introduced in place of the terminal methyl group of the hydrocarbon chains to improve aqueous solubility of the surfactant molecules. Figures 5.5 (a, b) show the free energy profiles of quat-10-OH and quat-16-OH molecules along with the free energy profiles of quat-10 and quat-16 molecules. The increase in the free energies is observed for the molecules can be measured by using the relation:

$$\Omega = e^{-\Delta F/_{k_B T}} \tag{5.5}$$

where Ω is the probability of a state with a free energy of ΔF . A decrease of $\Delta F = -4.8 k_B T$ and $\Delta F = -4.3 k_B T$ for the quat-10 and quat-16 molecules, therefore, amounts to an increase in the solubility tendency of the quat molecules by $\Omega \approx 122$ and 74 times respectively; an enormous increase in the solubility tendency is gained upon introduction of a single hydroxyl group.



Figure 5.5. Free energy profiles of (a) quat-10-OH and quat-10, (b) quat-16-OH and quat-16 molecules with respect to the distance of their center-of-mass from the air-water interface, ξ . The size of the error bars of the free energy profiles are smaller than the size of the markers.

The idea is based on the importance of hydroxyl groups in forming hydrogen bonds with water [142, 143]. While Zhao, *et al.*, and Wang, *et al.*, have already reported gain in the aqueous solubility upon addition of hydroxyl group to the head group [142, 143], Arachchi, *et al.*, have not found any incremental gain in aqueous solubility [107] [refer to Figure 5.6 for structures of the studied molecules]. One reason could be that, since they added the hydroxyl group right next to the oxyethylene group, which itself is a bigger polar moiety, there is no space for extra water molecules to approach the hydroxyl group. In this work, the hydroxyl group is added to the terminal position of the hydrocarbon tail instead to the head group. With this methodology, the interaction
strength of polar head groups of surfactant molecules with the desired surfaces remains undisturbed. Addition of a hydroxyl group to the terminal end of alkyl tail preserves the hydrophobic tail length, while enhancing the aqueous solubility of the molecule.



Figure 5.6. Structures of the molecules studied by Arachchi, *et al.*, for estimating the effect of hydroxyl group in aqueous solubility of the molecules [107]. No gain in the aqueous solubility is observed upon addition of the hydroxyl group to the oxyethylene group.

Figures S11 (a, b) [Supporting Information, Appendix D] show how the hydroxyl group aids in bringing the hydrophobic tails of the quat-OH molecules towards the water. The spatial and orientational distributions of the quat-OH molecules are shown in Figures S12/S13 [Supporting Information, Appendix D]. The application of enhanced solubility of the quat molecules is further identified by observing their micellization tendency in the bulk aqueous phase.

5.3.4 Micellization Tendency of Quat-OH Molecules

It is previously found in the MD simulations that quat-10 molecules, when randomly inserted in bulk aqueous phase, form a stable spherical micelle of size of 18 number of molecules [66, 73]. It is found that the free energy of micellization of 18 number of cationic surfactant molecules is strongly favorable and is estimated to be -68 k_BT [72]. This micelle experiences a free energy barrier of ~5 k_BT to adsorb onto the metal-water interface and does not adsorb in an unbiased MD simulation [66, 73]. The inability of surfactant molecules to adsorb onto the metal-water interfaces leads to a tremendous corrosion control cost, mainly for thousands of miles of oil pipelines. In this section, the micellization tendency of quat-10-OH molecules is determined. Figure 5.7 (a) shows the initial configuration of the quat-10-OH molecules placed in a bulk aqueous solution. A total of 18 quat-10-OH molecules are arranged close to one another and the counter-ions are placed close to the cationic head groups. The total number of water molecules is 4073 and the simulation box size is ~50 Å x 50 Å X 50 Å. MD simulation of the system is then performed in an NPT ensemble (fixed number of atoms, pressure, and temperature) for 50 ns. Figure 5.7 (b) shows the final configuration of the system. The quat-10-OH molecules are found to disaggregate in the aqueous phase.



Figure 5.7. (a) Initial configuration of the 18 number of quat-10-OH molecules arranged in a single aggregate. (b) Final configuration of the quat-10-OH molecules after a MD simulation of 50 ns. The red beads represent the polar head groups, the yellow beads represent the hydrophobic alkyl tails, the green beads represent the hydroxyl groups, the blue beads represent the chloride counter-ions and the small cyan dots represent the water oxygen atoms.

The *aggregation number* of the quat-10-OH molecules during the MD simulation is calculated. The aggregation number is defined as the number of quat-10-OH molecules comprising the largest aggregate of the system. Therefore, in the initial configuration, the aggregation number is 18. Figure 5.8 (a) shows the aggregation number of the molecules. Interestingly, the initial aggregate is found to disintegrate into the discrete molecules within the first 10 ns of the MD simulation. The quat-10-OH molecules stay in the aggregation number of ~2 for rest of the 40 ns, without showing any tendency to reaggregate further. The radial distribution function (RDF) is calculated between the oxygen atoms of the quat-10-OH molecules and the water molecules [see Figure 5.8 (b)]. A peak in the RDF indicates that there is a strong hydrogen bonding between the hydroxyl group of the quat-10-OH molecules and the water molecules. For comparison, the RDF between the nitrogen atoms of the surfactant molecules and the water molecules is also plotted. The presence of a strong peak in the O-O RDF, therefore, supplements the understanding of why the quat-10-OH molecules are successful in not forming micelles.



Figure 5.8. (a) Aggregation number of the system during the MD simulation. The aggregate is identified by utilizing the density-based spatial clustering of applications with noise (DBSCAN) algorithm. (b) RDF between the oxygen/nitrogen atoms of the quat-10-OH molecules and the oxygen atoms of the water molecules.

5.3.5 Free Energy of Micellization of Amine-10 Molecules

The micellization free energy of the amine-10 molecules is determined using the hydration free energies of single amine-10 molecules and a rigid amine-10 micelle. The method is described in a flowchart in Figure 5.9 (a).



Figure 5.9. (a) Schematics depicting a flowchart for determining the micellization free energy of amine-10 micelle. (b) Simulation system for obtaining the hydration free energy of a rigid amine-10 micelle.

The free energy of micellization of *n* number of amine-10 molecules can be written as:

$$\Delta F_{micellication} = \Delta F_{a/w}^{micelle} - n\Delta F_{a/w}^{molecule} + \Delta F_a^{micellization}$$
(5.6)

where $\Delta F_{a/w}^{micelle}$ is the hydration free energy of a rigid amine-10 micelle comprising of *n* number of amine-10 molecules, $\Delta F_{a/w}^{molecule}$ is the hydration free energy of an amine-10 molecule, and $\Delta F_a^{micellization}$ is the free energy of amine-10 molecules forming a hypothetical micelle in the air phase. $\Delta F_{a/w}^{molecule}$ is obtained in the section 3.2 and equals $7.5 \pm 0.33 k_B T$. Before discussing the estimation of $\Delta F_a^{micellization}$, the calculation of $\Delta F_{a/w}^{micelle}$ is described. $\Delta F_{a/w}^{micelle}$ is obtained for a rigid amine-10 micelle using the same umbrella sampling method as is used for obtaining the free energies of the single molecules in the previous sections. The simulation system for generating the free energy profile of the rigid amine-10 micelle is shown in Figure 5.9 (b). The simulation box size is 66.35 Å X 64.96 Å X 110.00 Å, and the total number of water molecules in the system is 9761. In the rigid micelle, the interactions between all the constituent atoms are turned off, and the external forces and torques always act to the center-of-mass of the micelle. Therefore, there is no net displacement of the constituent atoms with respect to each other, and the entire micelle moves/rotates as a rigid body. The rigid micelle is created by selecting a configuration of the non-rigid micelle comprising of 18 number of amine-10 molecules which has approximately the same values of squared radius of gyration and asphericity as the averaged values of the non-rigid micelle in the bulk water [73]. The purpose of choosing a rigid micelle is to make sure that the micelle remains intact across the air-water interface. In contrast, a non-rigid micelle remains intact in the bulk water but breaks apart at the air-water interface. The free energy and enthalpy profiles of the amine-10 micelle are shown in Figures 5.10 (a, b).



Figure 5.10. (a) Free energy profile, and (b) enthalpy profile of the rigid amine-10 micelle with respect to the distance of its center-of-mass from the air-water interface, ξ . The free energy of hydration, $\Delta F_{a/w}$ and the enthalpy of hydration, $\Delta U_{a/w}$ of the micelle are indicated by the arrows. The size of the error bars of the free energy profiles are smaller than the size of the markers.

From Figures 5.10 (a, b), it is found that $\Delta F_{a/w} = 56 \pm 1 k_B T$, and $\Delta U_{a/w} = -62.6 \pm 5 k_B T$. Correspondingly, one gets $T\Delta S_{a/w} = -118.6 \pm 5.1 k_B T$. The enthalpic-entropic comparison to the hydration free energy $-|T\Delta S_{a/w}| > |\Delta U_{a/w}|$ signifies that the hydration of the amine micelle is entropically driven. In contrast, it is worth mentioning here that the hydration of large hydrophobic spherical solutes ($d \ge 2 nm$) is understood to be enthalpically driven [103, 105].

The theoretical estimation of $\Delta F_a^{micellization}$ is now discussed. $\Delta F_a^{micellization}$ is broken down into the enthalpic and entropic contributions as:

$$\Delta F_a^{micellization} = \Delta U_a^{micellization} - T \Delta S_a^{micellization}$$
(5.7)

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 $\Delta U_a^{micellization}$ is determined as the difference between the internal energy of a rigid micelle and the intra-molecular energies of all the constituent molecules, as follows: $\Delta U_a^{micellization} = \Delta U^{micelle} - n\Delta U^{molecule}$ (5.8)

The internal energy of the rigid micelle, $\Delta U^{micelle}$ is the summation of the intramolecular energies of the constituent molecules, and the inter-molecular interaction energies in between the constituent molecules. $\Delta U^{molecule}$ is the ensemble-averaged intra-molecular energy of a molecule in infinite dilution. For the rigid micelle comprising of n = 18 molecules, it is found that $\Delta U_a^{micellization} = -355.8 \pm 2.1 k_BT$.

The entropy of micellization, $T\Delta S_a^{micellization}$ is calculated as:

$$T\Delta S_a^{micellization} = -k_B T \ln \left[\frac{q^{micelle}}{\left(q^{molecule}\right)^n / n!} \right]$$
(5.9)

where $q^{micelle}$ is the rotational partition function of the rigid micelle, and $q^{molecule}$ is the rotational partition function of an amine molecule. Since the rigid amie-10 micelle is nearly spherical in shape [73], its rotational partition function is considered to be given by the rotational partition function of a perfect sphere as follows [144-146]:

$$q^{micelle} = \sqrt{\pi \left(\frac{16MR^2 \pi^2 k_B T}{5h^2}\right)^3}$$
(5.10)

where M, R, and h are the mass of the rigid micelle (M = 2826 g/mol), radius of the rigid micelle (R \approx 1.5 nm), and Planck's constant, respectively.

Since the amine molecules are linear, their rotational partition function is considered as that of a rigid rod as follows [144-146]:

$$q^{molecule} = \frac{2\pi^2 m L^2 k_B T}{3h^2}$$
(5.11)

where m and L are the mass (m = 157 g/mol) and length (L \approx 1.5 nm) of an amine molecule.

By plugging in these values, one can obtain $T\Delta S_a^{micellization} = -134.4 k_B T$, implying that the entropy of aggregation of molecules into a micellar shape in the air phase is unfavorable, as expected.

From the computed values of $\Delta U_a^{micellization}$ and $T\Delta S_a^{micellization}$, one can obtain $\Delta F_a^{micellization} = -221.4 \ k_B T \pm 2.1 \ k_B T$. Using $\Delta F_{a/w}^{micelle}$, $\Delta F_{a/w}^{molecule}$, and $\Delta F_a^{micellization}$, one obtains $\Delta F_{micellication}$ from equation (5.6) as $\Delta F_{micellication} = -300.4 \pm 2.7 \ k_B T$.

A large value of the micellization free energy implies that micellization of amine-10 molecules in the bulk aqueous phase is highly favorable. Though some theoretical assumptions are made in the calculation of $T\Delta S_a^{micellization}$, the calculated $\Delta F_{micellication}$ lies within the same ballpark of the micellization free energy value of $-68 k_B T$ obtained for the charged imidazolinium micelle [72]. The uncharged amine molecules are expected to have more favorable free energy of micellization because of the absence of coulombic repulsions between the polar head groups unlike in the case of imidazolinium micelle which is comprised of the cationic molecules.

5.4 Conclusions

Numerous studies have been performed to understand how solubility of surfactant molecules is affected by their hydrophobic lengths, however, only a few studies have been performed in a methodical approach to understand the effect of polar head groups. As a result, a rational approach to designing a robust surfactant molecule has never been achieved. In this work, the role of charged and uncharged polar head groups is studied to determine the free energy and enthalpy of aqueous solubility of surfactant molecules of two different hydrophobic tail lengths. It is then proposed that addition of a hydroxyl group to the terminal position of the alkyl tails of the cationic quat molecules enhances their tendency of aqueous solubility by around two orders of magnitude. Besides improving the aqueous solubility, the hydroxyl group is proved successful in preventing the formation of micelles, which otherwise have a strong free energy of formation. In the end, the hydration free energy calculation methodology is utilized to determine the micellization free energy of uncharged amine molecules. The scope of this work can be extended further to design robust surfactant molecules with high aqueous solubility and reduced micellization tendency.

Chapter 6: Conclusions and Future Work

The aim of this research work has been to understand how the surfactant molecules, that are representative of those used in corrosion inhibition, adsorb onto metal-water interfaces and attain equilibrium adsorption morphologies. For this objective, advanced MD simulations have been performed to obtain the free energy of surfactant molecules in different states. The results of this work are summarized below.

6.1 Summary of Results

- Adsorption of surfactant molecules and surfactant micelles is studied. It is found that surfactant molecules adsorb strongly to the metal surface without any free energy barrier. Adsorption of surfactant micelles is, however, different for charged surfactants and uncharged surfactants. While the micelles of uncharged surfactant molecules undergo a barrier-less adsorption to the metal surface, the micelles of cationic surfactant molecules experience a long-range free energy barrier to adsorption on to the metal surface. This free energy barrier is associated with the interaction of the solvation shell of counter-ions surrounding the micelle and the adsorbed layers of water on the metal surface. In the adsorbed state, the micelles are thermodynamically most stable.
- A modified umbrella sampling methodology is developed to estimate the equilibrium adsorption morphology of surfactant molecules at the metal-water interface. Using this methodology, equilibrium adsorption morphologies of cationic, uncharged, and anionic molecules as well as their mixtures is studied. It

is found that the equilibrium adsorption morphology of cationic molecules varies with their alkyl tail lengths. Cationic molecules with short tail lengths (C-4) adsorb in a sparse monolayer of molecules lying flat onto the surface, whereas the molecules with long tail lengths (C-12) adsorb in a mixed morphology such that some molecules lie flat on the surface and the rest of the molecules are aggregated as hemi-micelles on the surface. As opposed to the cationic molecules, uncharged molecules (decanethiol) adsorb in a much more densely packed morphology forming a bilayer on the surface. An equimolar mixture of cationic and anionic molecules shows a synergistic effect by adsorbing in a much more densely packed morphology than cationic molecules. Because of forming dense adsorption morphologies, decanethiol molecules prove to be the most effective in excluding water from the metal surface, followed by the mixture of cationic and anionic molecules.

 Hydration free energies of linear alkanes ranging from methane to octadecane (C-18) are estimated for understanding the hydrophobicity of alkyl tail lengths of the surfactant molecules. It is found that the hydration of linear alkanes is governed by small length-scale hydrophobic effects, i.e., the hydration free energy of linear alkanes is entropically driven irrespective of the alkane length. This behavior is contrary to the hydration free energy of spherical solutes wherein there is a transition from entropically driven to enthalpically driven hydrophobic effects as the size of the solute increases. • Two desirable characteristics of surfactant molecules are their high aqueous solubility and small tendency towards micellization. In this regard, free energy of cationic and uncharged surfactant molecules across air-water interface is calculated. It is found that the addition of a hydroxyl group to the terminal position of the alkyl tail of the cationic surfactant molecules not only reduces the micellization of cationic molecules, but also enhances their solvation tendency by two orders of magnitude.

6.2 Future Work

6.2.1 Adsorption Behavior of Surfactant Molecules on Charged Surfaces

It is known that the metal surfaces get polarized in contact with the aqueous phase and carry a net charge on the surface. Also, there are studies which suggest that adsorption of counter-ions, such as bromides, on metal surface drives adsorption of cationic surfactant molecules. It is, therefore, important to accurately determine the charge of the metal surface and assign it to the metal lattice in the MD simulation.

6.2.2 Observation of Adsorption Morphology of Surfactant Molecules in Coarse-Grain MD Simulation

Adsorption morphology of surfactant molecules is determined on a metal surface area of ~ 5 nm x 5 nm. On such an area, adsorption of a maximum of ~ 100 surfactant molecules in a monolayer thickness is observed in the case of uncharged decanethiol molecules. It is therefore possible that the configuration of surfactant molecules is limited by a small size effect, and they may show a different adsorption morphology on a large surface area. Coarse-grain MD simulations of the surfactant molecules will thus be useful to predict their adsorption behavior on a large surface area.

6.2.3 Effect of Surface Roughness on Adsorption of Surfactant Molecules

In practical applications, a metal surface is never smooth but has some roughness. Understanding the effect of surface roughness on the adsorption morphology of surfactant molecules, therefore, may also be explored.

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Appendix A: Supporting Information for Chapter 2

Figure S1. Distribution of nitrogen (imid, quat, amine micelles) / carbon (triamine micelle) atoms of the head group around the center of mass of the micelles in the bulk aqueous phase: (a) imid-10 micelle, (b) quat-10 micelle, (c) amine-10 micelle, (d) triamine-10 micelle. The large peaks at ~10-13 Å indicate that the head groups are predominantly located at the periphery of the micelles. A small peak at ~4 Å in case of amine-10 micelle shows that some head groups are trapped within the core of the micelle.



Figure S2. Radial distribution function (RDF) of chlorides around the nitrogen atoms of the (a) imid-10 micelle, and (b) quat-10 micelle in the bulk aqueous phase. The larger peak in case of quat-10 is attributed to the presence of localized charge on the nitrogen atom, which in the case of imid-10 molecule is partially delocalized on the imidazoline ring.



Figure S3. Radial distribution function (RDF) between water-oxygen and chloride ions of the (a) imid-10 micelle, and the (b) quat-10 micelle in the bulk aqueous phase. The peaks around 3 Å and 5 Å show that the chloride ions are highly solvated with water molecules.



Figure S4. Density profile of water as a function of distance from the gold surface, ξ . Water is strongly adsorbed in two layers.



Figure S5. Normalized distribution of surfactant molecules in the equilibrium adsorbed state of (a) the imid-10 micelle, (b) the amine-10 micelle, and (c) the triamine-10 micelle. $\theta = 0^{\circ}$ indicates that the molecular axis is in plane of the metal surface. $\theta = +90^{\circ} / -90^{\circ}$ indicates that the molecule is standing with its polar head group pointing towards the metal surface or pointing towards the bulk aqueous phase respectively. The graph suggests that the molecules of triamine micelle stand-up on the surface, while those of other micelles lie flat on the surface.

Appendix B: Supporting Information for Chapter 3

Simulation Details

The umbrella sampling methodology, described in the main text, is employed to study the equilibrium adsorption morphology of five different surfactant systems — quat-12, quat-4, decanethiol, an equimolar mixture of quat-12 and pe-12, and an equimolar mixture of quat-12 and quat-4. The quat-12 and quat-4 simulations are performed for 50 surfactant molecules in an aqueous bath of \sim 7000 water molecules. Since the decanethiol molecules show significantly higher adsorption than the quat-molecules, the simulations are performed for 200 surfactant molecules in ~25000 water molecules. The simulations for mixture of quat-12 and pe-12 are performed for 50 surfactant molecules each in \sim 12400 water molecules. The simulations for the mixture of quat-12 and quat-4 are performed for 25 surfactant molecules each in ~6800 water molecules. The overall molar concentrations of the simulation systems are the same for all cases. In the simulations, the area of the x-y plane is kept fixed, but the height of the water column is changed to accommodate the different number of molecules. The heights of the *effective* water column for the five systems described above are 82 Å, 82 Å, 322 Å, 162 Å, and 82 Å respectively. The effective height corresponds to the height of the water column between the metal surface and the semi-permeable reflective wall placed at ~15 Å below the airwater interface.

In each umbrella sampling simulation, the system is equilibrated for the first 40 ns, and the next 40 ns are used for free energy calculations. For the free energy calculations, ξ_o is selected from 0 to N (total number of molecules in the system) in the

increments of 0.5, or 0.25 for the windows where the sampling is found to be insufficient. The *k* is chosen to be 25 kcal/mol, or 50 kcal/mol for the windows where there is insufficient sampling of ξ . The histograms of the umbrella sampling simulations of quat-12 system are shown in Figure S9.



Figure S1. Time series of ξ from unbiased MD simulations started at $\xi = 27.5$ (equilibrium morphology). The unbiased trajectory does not drift away to an appreciably different value of ξ in a 275 ns long simulation.



Figure S2. Snapshots of the simulations biased at (a) $\xi_o = 24$, (b) $\xi_o = 24.5$, (c) $\xi_o = 25$, (d) $\xi_o = 25.5$, (e) $\xi_o = 26$, (f) $\xi_o = 26.25$, (g) $\xi_o = 26.5$, (h) $\xi_o = 26.75$, (i) $\xi_o = 27$, (j) $\xi_o = 27.5$. The snapshots in (c) to (f) reveal that a water-solvated micelle is present in vicinity of the metal surface. The presence of this micelle is also captured in the red distribution profiles shown in Figure S3. The free energy barrier of ~4 k_BT at $\xi = 26.25$ in going from $\xi = 24$ to $\xi = 27.5$ [refer to Figure 3.2 (a), Main Text] is associated with the approach of water-solvated micelle towards the metal surface.[44, 66] Upon adsorption

of the micelle on the surface, as in (g)/(h)/(i)/(j), the free energy goes down because of the loss of solvation shell of water and counter-ions around the micelle and favorable surfactant-metal interactions [also see Figure S3] [44, 66].



Figure S3. Distribution profiles of center-of-mass of quat-12 molecules as a function of distance from the metal surface, *z* for different values of ξ_0 . The black curves represent the distribution of molecules in the adsorbed state, i.e., the molecules lying within one molecular length from the metal surface ($z \le 25$ Å). The red profiles represent the distribution of molecules in the bulk aqueous phase (z > 25 Å) for ξ_o in between $25 \le \xi_o \le 26.25$. These profiles capture the presence of a water-solvated micelle in the vicinity of the metal surface [also see Figures S2 (c, d, e, f)]. The blue profiles represent the distribution of molecules in the bulk aqueous phase (z > 25 Å) for $\xi_o = 24, 24.5$, 26.5, 26.75, 27, 27.5. These profiles capture the presence of a water-solvated micelle which is *not* in the vicinity of the metal surface [also see Figures S2 (a, b, g, h, i, j)].



Figure S4. Configurations of quat-12 molecules obtained from (a) an unbiased simulation run of 100 ns started with a random configuration, (b) a biased simulation at $\xi_o = 20$, and (c) a biased simulation at $\xi_o = 47$. The configuration at $\xi_o = 47$ is a planar monolayer where all the molecules are adsorbed in a standing-up orientation with their polar head groups on the metal surface [also refer to Figures S11 and S12 to compare the distributions of polar head groups and terminal methyl groups of quat-12 molecules as a function of distance from the surface, *z* for the configurations at $\xi_o = 47$ and $\xi = 27.5$ (equilibrium morphology)].

Table S1. Comparison of pairwise energies (Lennard-Jones plus Coulombic) of quat-12

and quat-4 molecules in the equilibrium morphology and the standing-up configuration

	quat-12		quat-4	
Pairwise interaction (LJ + Coulombic) energy (k_BT)	Equilibrium	Standing-up	Equilibrium	Standing-up
	morphology (ξ = 27.5)	configuration ($\xi_o = 47$)	morphology (ξ = 24)	configuration ($\xi_o = 47$)
Adsorbed surfactants — Adsorbed surfactants	11507 ± 58	39075 ± 199	5727 ± 28	39436 ± 209
Bulk surfactants — Bulk surfactants	6082 ± 36	N.A.	9626 ± 63	N.A.
Adsorbed surfactants — Bulk surfactants	7238 ± 47	N.A.	8240 ± 41	N.A.
Adsorbed surfactants — Bromides	-32647 ± 147	-84205 ± 463	-20774 ± 135	-81724 ± 400
Bulk surfactants — Bromides	-19906 ± 102	N.A.	-30188 ± 166	N.A.
Adsorbed surfactants — Surface	-2758 ± 15	-2577 ± 14	-1753 ± 9	-2480 ± 13
Bulk surfactants — Surface	0	N.A.	0	N.A.
Adsorbed surfactants — Water molecules	-3224 ± 17	-4334 ± 28	-2129 ± 11	-6034 ± 36
Bulk surfactants — Water molecules	-3754 ± 20	N.A.	-2595 ± 13	N.A.
Bromides — Bromides	24783 ± 136	37968 ± 190	24414 ± 125	36590 ± 165
Bromides — Surface	-8 ± 0.04	-41 ± 0.2	-8 ± 0.04	-44 ± 0.2
Bromides — Water molecules	-10441 ± 53	-4339 ± 24	-11710 ± 60	-4396 ± 22
Surface — Water molecules	-436 ± 2	-456 ± 3	-1129 ± 6	-537 ± 3
Resultant interaction energy per species (k_BT)	Equilibrium	Standing-up	Equilibrium	Standing-up
	morphology (ξ´ = 27.5)	configuration ($\xi_o = 47$)	morphology ($\xi = 24$)	configuration ($\xi_o = 47$)
Adsorbed plus Bulk surfactants	-6317 ± 41	-6483 ± 36	-5127 ± 27	-5683 ± 30
Bromides	-6718 ± 36	-6324 ± 38	-6926 ± 45	-6492 ± 39
Surface	-1601 ± 8	-1537 ± 10	-1445 ± 7	-1530 ± 7
Water	-8927 ± 40	-4564 ± 23	-8782 ± 45	-5484 ± 29

The table shows that the equilibrium morphology is favored by solvation of cationic surfactant molecules and their counter-ions by the water molecules (highlighted in green). The polar head groups and counter-ions in the equilibrium morphology are more water solvated than in the standing-up configuration [also refer to Figures S11, S13, S15, S16].



Figure S5. Distribution of orientation of (a) alkyl tails, and (b) aromatic rings of adsorbed quat-4 molecules on the metal surface. In (a), θ is the angle between the end-toend vector of the alkyl tails and the surface normal. The end-to-end vector is directed from nitrogen to the terminal methyl group of quat-4 molecule. In (b), φ is the angle between the vector normal to the aromatic rings and the surface normal. The distribution profiles are normalized by $\langle N \rangle \sin(\theta)$ and $\langle N \rangle \sin(\varphi)$ respectively, where $\langle N \rangle$ is the ensemble-average number of adsorbed molecules. A molecule is considered as adsorbed when its center-of-mass lies within one molecular length (~12 Å) from the metal surface. In (b), the presence of a single large peak in $0^{\circ} \langle \varphi \langle 30^{\circ}$ indicates that the aromatic rings lie flat onto the metal surface.



Figure S6. Distribution of orientation of alkyl tails of adsorbed decanethiol molecules present in the (a) first layer, and (b) second layer on the metal surface. θ is the angle between the end-to-end vector of the alkyl tails and the surface normal. The end-to-end vector is directed from thiol group to the terminal methyl group of decanethiol molecule. The distribution profiles are normalized by $\langle N \rangle \sin(\theta)$, where $\langle N \rangle$ is the ensemble-average number of adsorbed molecules in individual layers. A molecule is considered in the first layer when its center-of-mass lies within one molecular length (~14 Å) from the metal surface. If the center-of-mass falls within 14 Å $\langle z \leq 28$ Å, the molecule is considered in the second layer. The peak at $\theta \approx 0^{\circ}$ in (a) indicates that the molecules are aligned in standing-up orientation on the surface [also refer to Figure S17 (a)]. In the second layer, the peak at $90^{\circ} < \theta < 120^{\circ}$ indicates that the molecules are mostly aligned orthogonally to the surface normal [also refer to Figure S17 (b)]. The height of the bilayer is ~25 Å.


Figure S7. Distribution of orientation of alkyl tails of adsorbed (a) quat-12 molecules, and (b) pe-12 molecules in the equimolar mixture system of the molecules. θ is the angle between the end-to-end vector of the alkyl tails and the surface normal. The end-to-end vector is directed from the nitrogen/thiol group to the terminal methyl group of the molecules. The distribution profiles are normalized by $\langle N \rangle \sin(\theta)$, where $\langle N \rangle$ is the ensemble-average number of adsorbed molecules of individual kind. A molecule is considered as adsorbed when its center-of-mass lies within one molecular length (~23 Å for both kinds) from the metal surface. A total of 43 number of molecules are adsorbed in equilibrium, consisting of 24 quat-12 molecules and 19 pe-12 molecules. The presence of large peaks within 0° $\langle \theta \rangle \langle 45^{\circ}$ in (a) and (b) imply that both kinds of molecules are mostly aligned towards the surface normal. The height of the adsorption morphology is ~20 Å.



Figure S8. Distribution of orientation of alkyl tails of adsorbed (a) quat-12 molecules, and (b) quat-4 molecules in the equimolar mixture system of the molecules. θ is the angle between the end-to-end vector of the alkyl tails and the surface normal. The end-to-end vector is directed from nitrogen to the terminal methyl group of the molecules. The distribution profiles are normalized by $\langle N \rangle \sin(\theta)$, where $\langle N \rangle$ is the ensembleaverage number of adsorbed molecules of individual kind. A molecule is considered as adsorbed when its center-of-mass lies within one molecular length (~23 Å for quat-12 and ~12 Å for quat-4) from the metal surface. A total of 26 number of molecules are adsorbed in equilibrium, consisting of 16 quat-12 molecules and 10 quat-4 molecules [also refer to Figure S18]. The distribution profiles show that although quat-12 molecules do not follow any ordered orientation, quat-4 molecules predominantly adsorb by lying flat on the surface.



Figure S9. Histograms of umbrella sampling simulations of quat-12 molecules in the range $18 \le \xi_o \le 47$.



Figure S10. Free energy profile, ΔF plotted with respect to number of adsorbed molecules, N for (a) quat-12, (b) mixture of quat-12 and pe-12. To obtain ΔF with respect to N, the probability distributions in ξ , $P(\xi)$ are redistributed in N using $P_N(N_0) = \int_{\xi} P(\xi)h(N_0|\xi) d\xi$, where $h(N_0|\xi)$ is the fraction of configurations for a given N, in which the value of N equals N_0 .[147] A molecule is considered as adsorbed when its center-of-mass lies within one molecular length (~23 Å) from the metal surface. The free

energy as a function of N, $\Delta F(N)$ is then computed using $F(N) = -k_BT \ln P(N)$. The free energy profiles in (a) and (b) show a similar trend as in Figures 3.2 (a) and 3.6 (a) [Main Text] respectively, confirming that ξ is strongly correlated to N. A free energy barrier at N = 24, 25 in (a) and a jagged profile in (b) is a result of insufficient sampling for certain values of N. Since the order parameter, N does not account for a micelle approaching the surface, no free energy barrier is expected to be present because of the adsorption of micelle in these profiles.



Figure S11. Distribution of the polar head groups of quat-12 molecules as a function of distance, *z* from the metal surface in (a) the equilibrium configuration ($\xi = 27.5$), and (b) the standing-up configuration ($\xi_o = 47$). A broad distribution of head groups in the bulk aqueous phase in (a) corresponds to a micelle present in bulk aqueous phase [refer to Figure 3.2 (b), Main Text]. Quat-12 molecules are not present in the bulk aqueous phase in the standing-up configuration at $\xi_o = 47$ [refer to Figure S4 (c)].



Figure S12. Distribution of terminal methyl groups of the alkyl tails of quat-12 molecules as a function of the distance, *z* from the metal surface in (a) equilibrium configuration ($\xi = 27.5$) and (b) standing-up configuration ($\xi_o = 47$). A large peak at z = 20 Å (~molecular length) in (b) confirms that the molecules are standing-up on the metal surface.



Figure S13. Distribution of polar head groups of quat-4 molecules as a function of distance, z from the metal surface in (a) the equilibrium configuration ($\xi = 24$), and (b) the standing-up configuration ($\xi_o = 47$). A broad distribution of head groups in the bulk aqueous phase in (a) corresponds to the quat-4 molecules present in bulk phase [refer to Figure 3.4 (b), Main Text]. A sharp drop in the distribution profile in (a) at z = 82 Å is because of the presence of semi-permeable reflective wall kept at z = 82 Å.



Figure S14. Distribution of terminal methyl groups of the alkyl tails of quat-4 molecules as a function of distance, z from the metal surface in (a) equilibrium configuration ($\xi =$ 24), and (b) the standing-up configuration ($\xi_o = 47$). A broad distribution of head groups in the bulk aqueous phase in (a) corresponds to the quat-4 molecules present in bulk phase [refer to Figure 3.4 (b), Main Text]. A sharp drop in the distribution profile in (a) at z = 82 Å is because of the presence of semi-permeable reflective wall kept at z = 82 Å.

A large peak at z = 12 Å (~molecular length) in (b) indicates that the molecules are standing-up on the metal surface.



Figure S15. Distribution of bromide counter-ions of quat-12 molecules as a function of distance, *z* from the metal surface in (a) equilibrium configuration ($\xi = 27.5$), and (b) standing-up configuration ($\xi_o = 47$). Bromides are found in vicinity of polar head groups. In (a), bromides are also present in the bulk aqueous phase whereas in (b), the bromides are predominantly present at the metal surface [also refer to the distribution of polar head groups of quat-12 molecules in Figure S11 (b)]. A sharp drop in the distribution profile in (a) at z = 82 Å is because of the presence of semi-permeable reflective wall kept at z = 82 Å.



Figure S16. Distribution of bromide counter-ions of quat-4 molecules as a function of distance, *z* from the metal surface in (a) the equilibrium configuration ($\xi = 24$), and (b) standing-up configuration ($\xi_o = 47$). Bromides are found in vicinity of the polar head groups. In (a), bromides are also present in the bulk aqueous phase whereas in (b), the bromides are predominantly present at the metal surface [also refer to the distribution of polar head groups of quat-4 molecules in Figure S13 (b)]. A sharp drop in the distribution profile in (a) at *z* = 82 Å is because of the presence of semi-permeable reflective wall kept at *z* = 82 Å.



Figure S17. Distribution of the thiol groups and the terminal methyl groups as a function of distance, z from the metal surface in the (a) first adsorption layer, and (b) second adsorption layer of the equilibrium adsorbed morphology ($\xi = 161$) of decanethiol molecules.



Figure S18. Comparison of ΔF as a function of the adsorption number function, ξ of quat molecules near the metal-water interface. The profile of an equimolar mixture of quat molecules lies in between the profiles of pure quat molecules. Consequently, the number of adsorbed molecules in quat-12, quat-4 and the mixture systems at equilibrium are 30, 19 and 26 respectively.

Appendix C: Supporting Information for Chapter 4

The interaction potential between the surface at z = 0 and the oxygen atoms of water molecules is taken as a 9-3 potential:

$$U(z) = \varepsilon \left[\frac{2}{15} \left(\frac{\sigma}{z} \right)^9 - \left(\frac{\sigma}{z} \right)^3 \right], \qquad z < z_c$$
(S1)

where $\varepsilon = 1.0$ kcal/mol, $\sigma = 2.0$ Å are the potential parameters, z is the distance of an oxygen atom from the bottom surface, and $z_c = 5.0$ Å is the cutoff distance for the interaction potential. The density profile of water as a result of this interaction potential is shown in Figure S1.



Figure S1: Density of water as a function of the distance from the bottom surface, *z* for the simulation box of size of (a) 20 Å x 20 Å x 60 Å, and (b) 52.61 Å x 52.61 Å x 80 Å. In both the profiles, the vertical dotted line signifies the air-water interface where the density of water is 0.5 g/cc. The interface is labeled as $\xi = 0$ Å. Therefore, the region

within $\xi < 0$ Å corresponds to water, and the region within $\xi > 0$ Å corresponds to air. The peaks in the water density in the vicinity of the bottom surface are the results of the attractive interaction between water and the surface.



Figure S2: Intramolecular energy, U^{alkane} of alkanes as a function of the distance of their center-of-mass, ξ from the air-water interface. The intramolecular energies do not change across the air-water interface, signifying that the alkanes do not undergo any conformation change upon hydration [110].



Figure S3: Distribution of orientation of (a) C-6, and (b) C-18 in air, water, and near the interface ($\xi = 2$ Å). At $\xi = 2$ Å, the alkanes are adsorbed at the air-water interface, which is their most stable state ($\Delta F = 0$). θ is the angle between the end-to-end vector of the alkanes and the interface normal. The end-to-end vector joins the terminal methyl groups of the alkanes. The distribution profiles are normalized by $\sin(\theta)$. The uniform distributions of blue and red profiles indicate that the alkanes sample all the orientations in air and water. A large peak in the black profiles with $60^\circ < \theta < 90^\circ$ shows that the alkanes lie parallel when they are adsorbed at the interface.



Figure S4: Comparison of the free energy profile, ΔF with the interfacial energy, $\gamma \Delta A$ as a function of ξ for (a) C-1, (b) C-2, (c) C-3, (d) C-4, (e) C-5, (f) C-6, (g) C-8, (h) C-10, (i) C-12, (j) C-14, (k) C-16, (l) C-18. A bulge in the interfacial energy profiles (mainly for small alkanes – C-1 to C-8) is observed at the maxima of the profiles. The explanation of this bulged region is given in Figure S5 [Supporting Information].



Figure S5: Snapshots of the air-water interfaces for (a) C-3 at $\xi_0 = -9$ Å, (b) C-3 at $\xi_0 =$ -4 Å, (c) C-3 at $\xi_0 = 9$ Å, (d) C-2 at $\xi_0 = -9$ Å, (e) C-2 at $\xi_0 = -4$ Å, (f) C-2 at ξ 9 Å. In (a), two interfaces are present. The air-water interface is present at $\xi = 0$ Å and another interface (akin to an air-water interface) is present at $\xi = -9$ Å which encloses the C-3 molecule. In (b), only the air-water interface is present at $\xi = 0$ Å. However, the air-water interface has a protrusion in the downward direction up to $\xi = -5$ Å because of the presence of C-3 at $\xi_0 = -4$ Å (shown by an arrow). It turns out that the area of this interface is more than the total area of two interfaces in (a). This explains why the interfacial energy for $\xi_0 = -4$ Å is larger than for $\xi_0 = -9$ Å. In (c), only the air-water interface is present because C-3 is in the air; therefore, the interfacial energy for $\xi_0 = 9$ Å is the least. In (d), only the air-water interface is present at $\xi = 0$ Å. There is no interface corresponding to the C-2 molecule at $\xi_0 = -9$ Å because C-2 is not large enough to displace enough water upon hydration. In (e), however, the air-water interface has a protrusion in the downward direction up to $\xi = -4$ Å because of the presence of C-2 at $\xi_0 = -4$ Å (shown by an arrow). In (f), only the air-water interface is present because C-2 is in the air. For C-2, the interfacial energy for $\xi_0 = -9$ Å and $\xi_0 = 9$ Å are nearly the

same because both have only the flat air-water interface. The interfacial energy for $\xi_0 = -4$ Å is, however, larger because of the extra protruded area. A comparison of (a) and (d) shows that interfacial energy is generated only upon hydration of alkanes of size C-3 or larger.

Appendix D: Supporting Information for Chapter 5

The interaction potential between the water oxygens and the wall at z = 0 is considered as

$$U(z) = \varepsilon \left[\frac{2}{15} \left(\frac{\sigma}{z} \right)^9 - \left(\frac{\sigma}{z} \right)^3 \right], \qquad z < z_c$$
(S1)

where $\sigma = 2.0$ Å, $\varepsilon = 1.0$ kcal/mol, z is the distance of an oxygen atom from the wall at z = 0, and $z_c = 5.0$ Å is the cutoff distance for the interaction potential. The density profile of water because of this interaction potential is shown in Figure S1.



Figure S1. Water density as a function of distance from the bottom wall, z for the simulation box of size of 52.61 Å x 52.61 Å x 85 Å. The vertical dotted line indicates the air-water interface where the density of water is 0.5 g/cc. The interface is labeled as $\xi = 0$ Å. Therefore, the region within $\xi < 0$ Å corresponds to water, and the region beyond

 $\xi > 0$ Å corresponds to air. The peaks in the water density in the vicinity of the bottom surface are the results of the attractive interaction between water and the surface.



Figure S2. Comparison of free energy profiles of quat-10 and quat-16 molecules. In the aqueous phase, quat-16 has a higher free energy because of its longer hydrophobic tail. In the air, quat-16 has a lower free energy because at the same center-of-mass location (ξ), the polar head group of quat-16 molecule remains more submerged in the water as compared to that of the quat-10 molecule.



Figure S3. Snapshot of simulation box for (a) quat-10 molecule at $\xi = 16$ Å (air), (b) C-10 molecule at $\xi = 16$ Å (air), (c) quat-10 molecule at $\xi = -1$ Å (free energy minimum location), (d) C-10 molecule at $\xi = 2$ Å (free energy minimum location). The red beads represent the polar head group of the molecules, the yellow beads represent the hydrophobic alkyl tails, the blue bead represents the chloride counter-ions, and the small cyan dots represent the water oxygens. In (a), the air-water interface is increased because of the presence of cationic polar head group in the vicinity. In (b), no increase in air-water interfacial area is observed. In (c), the polar head group is submerged inside the water, while the hydrophobic tail protrudes outside the water [also refer to Figure S4 (a)]. In (d), the alkane lies parallel to the air-water interface and does not enter the aqueous phase.



Figure S4. Distributions of nitrogen of polar head group and carbon of terminal methyl group of (a) quat-10, and (b) quat-16 molecules when they are present at the air-water interface. z is the distance from the bottom wall of the simulation box. The polar head groups remain submerged inside the water, while the hydrophobic tail protrudes outside the water. The water distribution is plotted as $1/20^{\text{th}}$ of its density in g/cc.



Figure S5. Distribution of orientation of (a) quat-10, and (b) quat-16 molecules in bulk water and at the interface. Θ is the angle between the interface normal and the vector joining the nitrogen of the polar head group to the carbon of the terminal methyl group. In bulk water, the molecules sample all the orientations; at the interface, the molecules are inclined and sample fewer orientations – $30^{\circ} \leq \theta \leq 60^{\circ}$ for quat-10 and $45^{\circ} \leq \theta \leq$ 75° for quat-16. The profiles are normalized by sin (θ).



Figure S6. Distribution of orientation of C-10 molecule at the interface. Θ is the angle between the interface normal and the vector joining the terminal carbon atoms. A peak at $\theta \approx 90^{\circ}$ shows that C-10 lies flat onto the interface.



Figure S7. Comparison of the free energy profile of amine-10 molecule with those of quat molecules. quat molecules show good aqueous solubility and poor affinity for air, whereas the amine molecule shows better affinity for air than water. Also, the free energy profiles of quat molecules have a long-range convexity in the air ($\xi > 0$ Å), whereas the amine molecule does not show such a long-range convexity [also refer to Figure S8].



Figure S8. Snapshot of simulation box for the amine-10 molecule at (a) $\xi = 16$ Å (air), and (b) $\xi = 2$ Å (free energy minimum location). Unlike the quat molecules, the uncharged amine molecule does not pull water molecules towards itself when present in air. This is the reason why the free energy profile of amine-10 molecule does not increase sharply beyond $\xi > 0$ Å [also refer to Figure S7]. At the interface ($\xi = 2$ Å), the polar head groups remain solvated with water.



Figure S9. (a) Distributions of nitrogen of polar head group and carbon of terminal methyl group of amine-10 molecule at the air-water interface. *z* is the distance from the bottom wall of the simulation box. The water distribution is plotted as $1/20^{\text{th}}$ of its density in g/cc. (b) Distribution of orientation of amine-10 molecule at the interface. Θ is the angle between the interface normal and the vector joining the nitrogen of the polar head group to the carbon of the terminal methyl group. The figure (a) shows that the polar head of the amine-10 molecule is not as much submerged in water as the head groups of the quat molecules do [also refer to Figures S4 (a, b)]. The figure (b) shows that amine-10 molecule does not follow a preferred orientation unlike the quat molecules [also refer to Figures S5 (a, b)].



Figure S10. Enthalpic-entropic contributions to the free energy for alkane molecules and the amine-10 molecule. The comparison of the thermodynamic properties of amine-10

molecule with C-11 is useful to understand the effect of nitrogen in enhancing the tendency for hydration.



Figure S11. Simulation snapshot of (a) quat-10-OH, and (b) quat-16-OH molecules at the interface. The hydroxyl groups, as represented by the green beads, show a good affinity for water and aid in bringing the hydrophobic tails towards the water. Also refer to the simulation snapshot of quat-10 molecule in Figure S3 (c) for comparison.



Figure S12. Distributions of nitrogen of polar head group and oxygen of hydroxyl group of (a) quat-10-OH, and (b) quat-16-OH molecules when they are present at the air-water interface. z is the distance from the bottom wall of the simulation box. The hydroxyl groups are more submerged in water than the terminal methyl groups of quat molecules [also refer to Figures S4 [a, b] for comparison]. The water distribution is plotted as $1/20^{\text{th}}$ of its density in g/cc.



Figure S13. Distribution of orientation of (a) quat-10-OH, and (b) quat-16-OH molecules at the interface. The distribution of orientation of quat molecules are also shown here for comparison. Θ is the angle between the interface normal and the vector joining the nitrogen of the polar head group to the oxygen/carbon of the hydroxyl/terminal methyl group. The shift in the orientation profiles towards $\theta = 90^{\circ}$ demonstrate that the quat-OH molecules show more affinity for water than the quat molecules. The profiles are normalized by sin (θ).



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