Full Length Article

A molecular dynamics study on the dependence of phase behaviors and structural properties of two-dimensional interfacial monolayer on surface area

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A B S T R A C T

The packing state and structure of monolayer at the air/water interface have important effect on its wide application. Using molecular dynamics (MD) simulation, phase transitions of sodium dodecyl sulfate (SDS) monolayer, dependent on the surface area per molecule, have been studied in the view of configuration entropy. With the reduction of surface area per molecule, three two-dimensional (2D) phases are defined, including gaseous, liquid expanded and liquid condensed phases. At small surface area per molecule, the 2D monolayer will collapse and 3D aggregates are formed in the bulk solution. We give a detailed description of the collapse mode from interfacial monolayer at the air/water interface to micelle in the solution at the molecular level. Using the quasi-harmonic (QH) approximation, the entropic change of SDS for 2D phase transition are first introduced, which is around $-29.7\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for the transition from 2D gaseous film to 2D liquid expanded film and $-42.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for the transition from 2D liquid expanded film to 2D liquid condensed film. The effect of different surface coverages on the dynamical and structural properties of SDS monolayer at the air/water interface is evaluated. Based on simulated results, a schematic diagram of 2D monolayer in different phases is proposed.

1. Introduction

Surfactants are the versatile industry products with annual millions of metric-tons yield, exhibiting the strong adsorption at the interface between two immiscible phases. Since the circumstance and force of surfactant at the interface are different from those in the bulk, the interfacial surfactant shows some particularly physical and chemical properties. These different properties play significant roles in many industrial and daily applications [1], *i.e.*, in foams, emulsions, detergency, heterogeneous catalysis, oil recovery, food and pharmaceutical fields. An understanding of interfacial systems has important meanings for the relevant advances in enhanced oil recovery, emulsions and foams [1].

The adsorption behaviors of surfactant molecules at the air/water interface have been an important part in research that aims to elucidate the interfacial science. Since interfacial region is very small relative to the bulk of solution, there exist challenges to study the properties of molecules at the interface [2]. A variety of techniques, including

surface tension measurements, infrared external reflection spectroscopy (IERS) [3], vibrational sum frequency spectroscopy (VCFS) [4], electrochemical microcalorimetry [5], and theoretical methods [6–8], are developed to characterize this adsorption phenomenon of surfactants. Using these methods, properties of films around saturated state, such as interfacial tension (σ), interfacial pressure (π), the alignment of surfactant molecules at the interface, conformation of molecules, and intermolecular interactions, are studied to describe and understand the surface monolayer as thorough as possible.

Due to the scientific and technological applications, sodium dodecyl sulfate (SDS) has been widely studied as one model surfactant [1,9–11] in colloid and interface research. Hore et al. [12] gave a detailed description of the orientation of sulfate head group at the air/water interface by the VCFS. Based on the measured surface tension and surface potential, Lunkenheimer et al. [13] found the odd-even effect of the cross-sectional area of homologous sodium n-alkyl sulfates (from C7 to C14) by a surface equation of state approach. Allen et al. [6] studied the effects of Li^+, Na^+, K^+, Cs^+, and NH_4^+ cations on the structural and

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interfacial properties of dodecyl sulfate films, proposing that interfacial monolayer can be modified by changing the counterion. Using molecular dynamics (MD) simulation, different configuration and orientation of SDS molecules under low surface coverage at the vapor/water and the CCl$_4$/water interface were compared [14]. It is found that SDS molecules are prone to bend lying at the air/water surface, while they are biased to the surface normal with larger proportion of trans-configuration at the oil/water interface.

Using experimental measurements, the isotherm of surface pressure-surface area per molecule (π-A$_{sa}$) can be obtained. This isotherm can be comparable to the one of pressure-volume (P-V) in three-dimensional (3D) space, which can denote the polymorphism of system. Similarly, the phase transition also exists for 2D monolayer system. According to the π-A$_{sa}$ isotherm, different phases for 2D system can be defined, such as 2D gaseous and liquid phases. With the tiny amount of molecules at the vapor/liquid interface (surface area per molecule is large), the gaseous (G) film is formed. Under this condition, different amphiphilic molecules have enough space to spread at the interface. The surface area per molecule is generally larger than $\sim 4\,nm^2$ [15,16]. Interactions between these molecules are so little that can be neglected, being similar to the 3D gaseous phase. As surface area per molecule decreases, the space for individual molecule is reduced, forming the liquid (L) film. Two types of liquid film [16–18], including liquid expanded (LE) and liquid condensed (LC) films, are defined. Both films pack with some gauche defects, but interactions between surfactant molecules become stronger. When the surface area per molecule continues decreasing, the transition from a loosely stacked to densely packed monolayer occurs. Surfactant molecules of this densely packed monolayer are with almost all-trans conformations and almost straightly orient to the air. This film is named as the condensed (C) film. If the surface area per molecule is further compressed beyond one critical point, surfactant molecules will be unstable at the interface. The monolayer will collapse, desorb from the surface and finally enter the bulk of solution with different clusters [19–22].

Both experimental and theoretical methods have been used to study the phase transitions of SDS monolayer. This adsorbed monolayer is assigned to the Gibbs monolayer, which can be comparable to the widely studied Langmuir monolayer [16–18]. It is formed by water-insoluble material and has more abundant morphologies than Gibbs monolayer. For SDS monolayers at the air/water interface, the effects of aqueous SDS concentration [3] and temperature [23] on the conformational orders and states of alkyl chains were studied using IERS and IR transmission spectra. As concentration increases, conformational order improves until the saturated adsorption. At this concentration, SDS molecules at the air/water interface were in liquid crystal state. A 2D phase transition from fluid state to solid state was found according to the shift in IR transmission spectra.

However, due to the thermodynamic equilibrium between interfacial monolayer and bulk phase [24], it is not easy to detect and define different phases of Gibbs monolayers from experiments as those of Langmuir monolayers. Molecular dynamics (MD) simulation as an effective tool is more convenient to study the behaviors of Gibbs monolayers to give explanations and supplements for the experimental observations. A possible transition from liquid to gas phases was found by Chen et al. [25] according to the structural changes via MD simulation. Morphologies and structural properties of monolayers at different surface areas per molecule were evaluated and compared [8] between hexaethylene glycol monododecyl ether and SDS surfactants at the vapor/water interface. A phase transition from gaslike to liquidlike phases was found with the evolution of surface concentration. Using MD simulation, the conformation of alkyl chain and interfacial properties of sodium alkyl sulfate surfactants were studied [20] with the change of alkyl length and surface concentration at the water/trichloroethylene (TCE) interface. Two phases (including G and LE phases) were found in their study. At small surface area per molecule, the monolayer collapse occurred, and a swollen micelle involving TCE

molecules was finally generated in bulk water.

Although gaseous and liquid phases of Gibbs monolayers are defined both from theoretical and experimental measurements, the thermodynamical information between different phases is deficient. Moreover, the definition of different phases of MD simulations is just based on the conformation of alkyl chains. In this paper, the aim is to give a systematical study on the effects of surface area per molecule on 2D phase behaviors of SDS monolayer from directly calculated configuration entropy of molecule with MD simulation. The entropy that directly measures the state and order of system is used to define different 2D phases. Since microscopic structures of the monolayer in different phases directly affect properties of the monolayer, the dependence of dynamical and structural information of monolayer on surface area will also be discussed.

2. Simulation details

2.1. Simulation method

The entropy of molecule is calculated via the QH approximation method proposed by Karplus et al. [26] With this method, the absolute entropy is connected with the covariance matrices of atomic fluctuations of molecule. Based on the sufficient sampling of MD trajectories, such fluctuation can be evaluated from the covariance matrix of Cartesian coordinates, finally yielding the configuration entropy by the following equation:

$$S_{QH} = R \sum_i \frac{\hbar\omega_i/k_B T}{\exp(\hbar\omega_i/k_B T)-1} - \ln[1-\exp(-\hbar\omega_i/k_B T)]$$

where k_B the is Boltzmann's constant, T the is temperature, $\hbar$ is the Planck's constant divided by 2π, and ω_i is the frequency of atom i. Here, the ω is calculated according to the formula,

$$\det\left(\mathbf{M}^{1/2}\sigma\mathbf{M}^{1/2} - \frac{k_B T}{\omega^2}\mathbf{1}\right) = 0$$

where $\mathbf{M}$ is the mass matrix and $\mathbf{1}$ is the unit matrix. The covariance matrix of the Cartesian coordinates, σ, is defined as:

$$\sigma_{ij} = \langle(x_i-\langle x_i\rangle)(x_j-\langle x_j\rangle)\rangle$$

2.2. Simulation details

Eight systems containing different amounts of SDS molecules were simulated using the Gromacs 4.6.7 package [27]. All atoms were described by the parameters generated from the automated force field topology builder [28,29] (ATB), which were compatible with the Gromos 53a6 parameters [30]. These parameters have been validated for the colloidal system [31–33] and can be directly used in the Gromacs. A Hessian matrix [34] was used to provide additional parameters according to the judgment that a bond exists if all three eigenvalues of the interatomic force constant matrix between any two atoms are positive. Initial charges of SDS molecules were estimated using the electrostatic potential (ESP) method [35]. The final charges and charge groups were assigned by the method of the ATB paper [28]. Water molecules were described by the single-point charge (SPC) model [36].

All simulations were begun with the preassembled system with two symmetric monolayers. The procedure for building initial configurations was introduced in the ESI. After constructing the initial model, the energy of system was minimized with the steepest descent method. Then, NVT simulations with adequate simulation length (at least 100 ns) were carried out at 298 K to equilibrate the system and obtain the production trajectories. To keep the constant temperature during the whole simulation, the v-rescale temperature coupling method [37] was used in all simulations. All bonds were constrained using the LINCS algorithm [38]. For nonbonded interactions, electrostatic interactions