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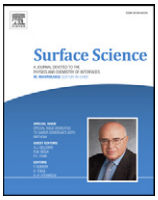

Interactions of water with the nonionic surfactant polyoxyethylene glycol alkyl ethers studied by phase-sensitive sum frequency generation and molecular dynamics simulation

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ABSTRACT

Phase-sensitive sum frequency generation (SFG) vibrational spectroscopy and molecular dynamics (MD) simulation were used to study the interactions between water molecules and the surfactant polyoxyethylene glycol alkyl ether ($C_{12}E_4$) at its critical micelle concentration. The surfactant enhanced the positive peak of water's SFG spectrum suggesting that $C_{12}E_4$ was more anionic-like, even though the surfactant was overall neutral. MD simulations showed that the surfactant increased the depth of the surface anisotropic layer from 0.31 to 1.82 nm and the average number of hydrogen bonds per water molecule from 2.7 to 3.1. For water molecules near the surfactant, their H and O atoms are confined in well-separated shells. Both the O and C atoms in the head group of the surfactant are surrounded by the H atoms, instead of the O atoms, of water indicating that the negatively charged O atoms of the surfactant play a more important role than the C atoms in determining the orientation of water. The simulation also showed that the orientation of surface water molecules was flipped in the presence of the surfactant, which was consistent with the observed SFG spectra.

1. Introduction

Nonionic polyoxyethylene glycol alkyl ethers are widely used in detergents [1], cosmetics [1], drug delivery [2], membrane proteins purification and crystallization [3], and pharmaceutical sciences [1] because of their detergency, wetting, and foaming properties. Polyoxyethylene glycol alkyl ethers with the chemical structure of C_mH_{2m+1}—$(OCH_2CH_2)_n$—OH are generally referred as C_mE_n with *m* denoting the number of carbon in hydrophobic carbon chain and *n* being the number the ethylene oxide units. Much work has been carried out to study the properties of surfactant aggregates in the solution phase [4–6]. However, a good understanding of an adsorbed layer on water surface is still lacking because it is technically challenging to probe water interfaces. Neutron reflection has been used to determine the structure of a monolayer of $C_{12}E_8$ adsorbed on water surface at its critical micelle concentration (CMC). It was found that there was a large average tilt of the surfactant molecules away from the surface normal [7]. In a later study, Lu et al. showed that the hydrocarbon chain in the $C_{12}E_m$ series where m ≤ 6 tilted at ~40° away from the surface normal [8].

Kuhn et al. used molecular dynamics (MD) simulations to study a $C_{12}E_5$ monolayer (0.55 nm^2/molecule) at the water surface and found the monododecyl chains had an average tilt angle of 43° at the CMC [9], which agrees with the neutron reflection measurement [8]. A more recent MD simulation of $C_{12}E_2$ adsorbed at the air/water interface (0.34 nm^2/molecule at the CMC) showed that the water molecules have a strong tendency to form hydrogen-bonded bridged structures with the oxygen atoms of the same surfactant chain [10]. Chanda et al. carried out an MD simulation for a monolayer of $C_{12}E_6$ (0.55 nm^2/molecule), showing that the surfactant monolayer strongly influences the translational and rotational mobility of interfacial water molecules [11]. Currently, a good understanding of the structural changes of water in the presence of polyoxyethylene glycol alkyl ethers is still lacking, and it is important to obtain a further microscopic understanding of the interaction between the surfactants and the interfacial water.

The current study uses phase-sensitive sum frequency generation (SFG) vibrational spectroscopy and MD simulations to study the interaction of water molecules with polyoxyethylene glycol alkyl ethers. SFG is known for its high surface sensitivity [12]. Recent developments in phase-sensitive SFG have allowed direct measurements of both the surface's vibrational resonances and the averaged orientation of the functional groups [13,14]. This new technique provides an opportunity to gain further molecular-level information at the water surface. In addition, MD simulation was used to obtain a detailed structure of water at the interface.

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2. Material and methods

2.1. Material and sample preparation

Tetraethylene glycol monododecyl ether (>98%) was purchased from Sigma–Aldrich. Water (resistivity > 18.2 MΩ · cm) used in the experiments was obtained from Millipore system. The 7×10^{-5} M surfactant solution was obtained by diluting the stock solution with water. The solutions were freshly prepared before measurements. All experiments were performed at 20 ± 0.5 °C and under 1 atmosphere pressure.

2.2. Phase-sensitive SFG setup

A femtosecond Ti-sapphire laser (120 fs, 800 nm, 1 kHz, and 2 mJ/pulse) was used to pump an optical parametric amplifier in order to generate a broad-band femtosecond IR beam. The IR beam and a narrow-band picosecond 800 nm beam were aligned collinearly with an incident angle of 60° [15,16]. A reference SFG was obtained by focusing the IR and picosecond 800 nm beams into a quartz crystal (thickness ~50 μm). The IR, 800 nm, and reference SFG beams were then focused again on the sample. The reference SFG and the SFG generated at the sample went through a time-delay, a polarizer, a band pass filter, a lens, and a monochromator, and then the interference pattern was recorded by a charge-couple device (CCD) camera. The polarization combination used in this study was SSP (s-polarized SFG, s-polarized 800 nm, and p-polarized IR). The energy of the 800 nm and IR beam were ~10 μJ/pulse and ~3 μJ/pulse, respectively. Spectra presented in the paper were acquired over a period of 20 min.

2.3. MD simulations

MD simulations were performed using GROMACS 5.0.2 [17–19] in the canonical ensemble. The all-atom force field proposed by Shen and Sun for polyoxyethylene glycol alkyl ethers was used for $C_{12}E_4$ [20]. The flexible extended simple point charge (SPC/E) model was used for water molecules [21]. The dimension of the simulation box was $3.6 \times 3.6 \times 32\ \text{nm}^3$. A slab of $3.6 \times 3.6 \times 7\ \text{nm}^3$ was filled with 3017 water molecules. This slab of water was placed at the center of the simulation box, and a vacuum of approximately 12.5 nm located on both sides of the water slab. Thirty $C_{12}E_4$ were randomly placed on each side of the water surface using the PACKMOL package [22]. The surface coverage was ~0.44 nm^2/molecule, which corresponds to the surface coverage of $C_{12}E_4$ with a CMC of 7×10^{-5} M [23]. The steepest descent energy minimization was conducted to prepare the system for the simulation. The temperature was maintained at 293 K using the V-rescale thermostat with the temperature constant, $\tau_T = 0.1$ ps [24]. All bonds were constrained by the SHAKE algorithm with a tolerance of 10^{-4} [25]. The Lennard–Jones interactions were truncated with a cutoff radius of 1.2 nm. Unlike-atom interactions were computed using the standard Lorentz-Berthelot combination rules [26,27]. Periodic boundary conditions were applied to all three directions. The particle-mesh Ewald (PME) algorithm with a cutoff radius of 1.2 nm and a grid spacing of 0.12 nm was used for the long-range columbic interactions [28]. The simulation was executed for 40 ns with a step of 2 fs for integrating the equations of motion. The system took 10 ns to reach equilibrium, and the following 30 ns were used to produce the results presented in the current study. The visualizations were made by VMD 1.9.1 [29].

The accuracy of the MD simulation was verified using the value of the surface tension. The surface tension was calculated by the indirect method developed by Kirkwood-Buff: [30]

$$\gamma = \frac{1}{2}\int_0^{L_z} \left(P_z - 0.5\left(P_{xx} + P_{yy}\right)\right) dz \qquad (1)$$

where L_z is the total length of the system, P_{xx} and P_{yy} are the parallel components of pressure tensor with respect to the surface, and P_{zz} is the perpendicular component. The energy and pressure tensor were recorded every 2 fs to integrate Eq. (1). We performed the simulation with 10 different initial configurations built by PACKMOL [22] and obtained a surface tension of 33.1 ± 1.40 mN/m, which was in reasonable agreement with our experimentally measured value of 29.6 ± 0.2 mN/m.

To determine hydrogen bonding, we used positional order based on the distance between O of acceptors with H of donors in the system [31]. Two molecules are assumed to be hydrogen bonded if they satisfy the following condition:

$$R_{O-H} < {R_{O-H}}^{Cutoff} \qquad (2)$$

The cutoff distance ${R_{O-H}}^{Cutoff}$ was derived from the radii of the first hydrogen atom shell. The cutoff distance between the O atoms of the surfactant and the H atoms of water was 0.20 nm for O1–O4 (defined in Fig. 3a) and 0.25 nm for O5 (defined in Fig. 3a). The cutoff distance between water's O atoms and water's H atoms was 0.22 nm. The terminal H atoms in $C_{12}E_4$ were also allowed to form hydrogen bond (HB) with water's O with a cutoff distance of 0.22 nm.

3. Results and discussion

Fig. 1a shows the SFG spectrum of pure air/water interface. The spectrum has two major distinguishable OH bands: a positive OH band near 3100 cm^{-1} and a negative OH band near 3450 cm^{-1}. For the OH symmetric stretch, the $\text{Im}(\chi^{(2)})$ can be positive or negative, depending on the sign of the OH projection with respect to the surface normal: a positive peak indicates water molecules with the hydrogen pointing toward the air (up), and a negative peak indicates the OHs pointing toward the bulk (down) [14,16,32]. It has been proposed that the low-frequency band is the result of a strongly hydrogen-bonded water structure while the high-frequency band is the result of a weakly hydrogen-bonded water structure [33,34]. However, the origin of the low-frequency peak has been controversial [35–37]. Tian et al. proposed that "ice-like" tetrahedrally bonded water molecules have a dominating contribution to the positive band at 3100 cm^{-1} [34]. Nevertheless, Nihonyanagi et al. attributed the positive peak to water dimers at the surface, which generates a vertical induced dipole pointing toward the air [38], rather than tetrahedrally coordinated water molecules. Experimentally, it was clearly demonstrated that the low-frequency peak has a negative sign when the water surface was occupied by cationic surfactants and a positive sign when the water surface was occupied by anionic surfactants [39–41]. It is generally accepted that the negative 3450 cm^{-1} peak is water molecules with their OHs pointing down. Nihonyanagi et al., using phase-sensitive SFG along with MD simulation, showed that the H-bonded OH groups near the surface, on average,

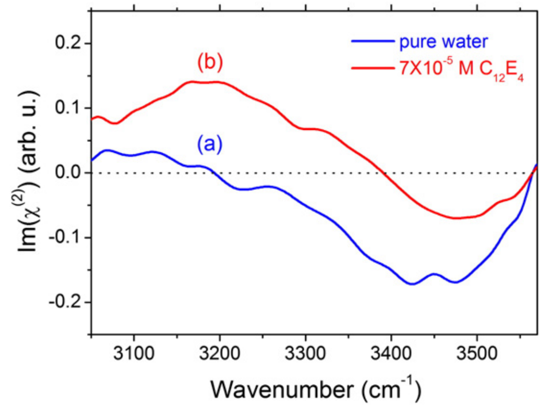

Fig. 1. $\text{Im}(\chi^{(2)})$ spectra of air/water interfaces with 0 M (a) and 7×10^{-5} M (b) of $C_{12}E_4$.