



CHAPTER III EXPERIMENTAL

3.1 Equipment and Materials

3.1.1 Equipment

Desktop computer (Intel® Core™ i7, CPU 860, 2.80 GHz, RAM 4 GB, Window 7, and Microsoft Office 2007)

3.1.2 Software

3.1.2.1 *GROMACS molecular dynamics simulation package, version 4.0.7*

3.1.2.2 *Visual Molecular Dynamics (VMD), version 1.9*

3.1.2.3 *Microsoft Visual Studio 2005*

3.1.2.4 *WinSCP*

3.1.2.5 *PuTTY*

3.2 Model

3.2.1 System Compositions

Extensive all-atom MD simulations of a four-component system, composed of water, dodecyl benzenesulfonate (SDBS), sodium ions, and SWNTs, were utilized to study the self-assembly of SDBS on the SWNT surface. Three SWNTs [(6,6), (12,12), and (20,20)], with diameters of 0.814, 1.628, and 2.713 nm, respectively, were considered.

To investigate the effect of surface coverage on the surfactant aggregate structure at the SWNT/water interface, two surface coverages were considered, 1.0 SDBS molecules/nm² (1.0 nm²/headgroup) and 2.8 SDBS molecules/nm² (0.357 nm²/headgroup). Both surface coverages are comparable to those known for SDS (Xu *et al.*, 2010). It should be noted that the surface coverages used in this study are much lower than those estimated from experimental adsorption isotherms [e.g., the packing density of the sulfonate headgroup was found to be 22.5

molecules/nm² by assuming the nanotube surface area of of 2000 m²/g (Matarredona *et al.*, 2003)]. Based on the results of this study, the surface density of 22.5 molecules/nm² appears a rather high estimate. In fact, as detailed below, even at the surface coverage of 2.8 SDBS molecules/nm², SDBS agglomerate into micellar aggregates away from the SWNT surface was observed. These results suggest that employing surface coverages higher than 2.8 molecules/nm² would result in the formation of micelle in the aqueous solution. Because of computational limitations, this study therefore was concentrated on low surface coverage (defined high and low surface densities below for simplicity). Other techniques, including dissipative particle dynamics (Angelikopoulos and Bock, 2009; Calvaresi *et al.*, 2009), should be employed to study larger surfactant densities.

Because SDBS surfactants are found with different molecular architectures (Myers, 2005), it is of interest to quantify the SDBS packing on SWNTs as a function of the SDBS molecular structure. Two different molecular architectures of SDBS were considered. In the first, benzene sulfonate was attached to the 12th carbon atom in the dodecane backbone (linear SDBS). In the second, the benzene sulfonate was attached to the 5th carbon atom in the dodecyl chain (branched SDBS). These structures are shown in Figure 3.1.

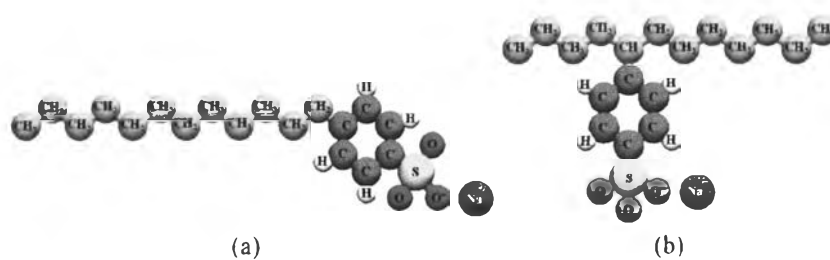


Figure 3.1 Chemical structures of (a) linear and (b) branched SDBS. Sodium ions are considered completely dissociated.

3.2.2 Force Fields

The carbon atoms within SWNTs were treated as Lennard-Jones (LJ) spheres and maintained fixed throughout the course of the simulations. The LJ

parameters used to describe carbon-carbon interactions were those of Cheng and Steele (1990).

Water molecules were modeled using the simple point charge-extended (SPC/E) model (Berendsen *et al.*, 1987).

One molecule of SDBS surfactant is composed of one hydrophobic tail of 12 carbon atoms (1 CH₃ and 11 CH₂ groups for linear SDBS; 2 CH₃, 9 CH₂, and 1 CH for branched SDBS) and one hydrophilic head composed of one benzene sulfonate group. The CH_n-groups in SDBS were modeled as united-atom LJ spheres (Martin and Siepmann, 1997; Siepmann *et al.*, 1993; Smit *et al.*, 1995). The benzene sulfonate was described by the explicit all-atom model using the DREIDING force field (Mayo *et al.*, 1990). The force field parameters used to calculate the intramolecular interactions were borrowed from Jang *et al.* (2004).

The total intramolecular potential was given by

$$E_{total} = E_{vdW} + E_Q + E_{bond} + E_{angle} + E_{dihedral} . \quad (1)$$

In Eq. (1), E_{total} , E_{vdW} , E_Q , E_{bond} , E_{angle} , and $E_{dihedral}$ are the total potential energy, van der Waals, electrostatic, bond-stretching, angle-bending, and dihedral-energy contributions, respectively.

A harmonic potential was used to model bond-stretching:

$$E_{bond} = K_b (r - r_0)^2 . \quad (2)$$

In Eq. (2), E_{bond} is the bond-stretching energy, K_b is the elastic constant, r is the instantaneous distance between the bonded atoms, and r_0 is the equilibrium distance between them.

All the angles in SDBS surfactants were constrained by harmonic potentials:

$$E_{angle} = K_\theta (\theta - \theta_0)^2 . \quad (3)$$

In Eq. (3), E_{angle} is the angle-bending energy, K_θ is the force constant, θ_0 and θ are the equilibrium and the instantaneous angles, respectively.

Dihedral angles were constrained through the Ryckaert and Bellemans potential:

$$E_{dihedral} = \sum_{k=0}^5 c_k \cos^k(\phi). \quad (4)$$

In Eq. (4), $E_{dihedral}$ is the dihedral energy, c_k are the energy constants, and ϕ is the dihedral angle. All force field parameters used to compute the intra- and intermolecular interactions are summarized in Table 3.1.

Table 3.1 Parameters used to implement the force fields in this study [eq. (2), (3), and (4)]

Lennard-Jones (σ and ϵ) and Electrostatic (Q) Interaction Potential Parameters			
Atom (or Groups)	σ (Å)	ϵ (kcal mol ⁻¹)	Q (e)
CH ₃	3.9300	0.2265	0.0000
CH ₂	3.9300	0.0934	0.0000
CH	3.3953	0.0934	0.0000
C* (in CH ₂ -C*-C-H)	3.4730	0.0951	-0.0556
C* (in CH-C*-C-H)	3.4730	0.0951	-0.0556
C* (in CH ₂ -C-C*-H)	3.4730	0.0951	-0.1133
C* (in CH-C-C*-H)	3.4730	0.0951	-0.1133
C* (in S-C*-C-H)	3.4730	0.0951	-0.1438
C* (in S-C-C*-H)	3.4730	0.0951	-0.0905
H* (in CH ₂ -C-C-H*)	2.8464	0.0152	0.0631
H* (in CH-C-C-H*)	2.8464	0.0152	0.0631
H* (in S-C-C-H*)	2.8464	0.0152	0.1069
S	3.5903	0.3440	1.1061
O	3.0332	0.0957	-0.6131
Na	2.8010	0.5000	+1.0000
H (in H ₂ O)	0.0000	0.0000	0.4238
O (in H ₂ O)	3.1660	0.1554	-0.8476
C (in SWNT)	3.4000	0.0557	0.0000

Table 3.1 (Cont.) Parameters used to implement the force fields in this study [eq. (2), (3), and (4)]

Bond-Stretching Potential Parameters		
Bond	K_b (kcal mol⁻¹ Å⁻²)	r_0 (Å)
CH ₃ -CH ₂	260.000	1.540
CH ₂ -CH ₂	260.000	1.540
CH ₂ -CH	260.000	1.540
CH ₂ -C	350.000	1.460
CH-C	350.000	1.460
C-C	525.000	1.390
C-H	350.000	1.020
C-S	350.000	1.480
S-O	350.000	1.480
O-H	N/A	0.945

Angle-Bending Potential Parameters		
Angle	K_θ (kcal mol⁻¹ rad⁻²)	θ_0 (deg)
CH ₃ -CH ₂ -CH ₂	62.095	114.000
CH ₂ -CH ₂ -CH ₂	62.095	114.000
CH ₂ -CH-CH ₂	62.095	114.000
CH ₂ -CH ₂ -C	109.491	124.193
CH ₂ -CH-C	109.491	124.193
CH ₂ -C-C	109.491	124.193
CH-C-C	109.491	124.193
C-C-C	109.491	124.193
C-C-H	109.491	124.193
C-S-O	115.500	175.000
O-S-O	115.500	175.000

Table 3.1 (Cont.) Parameters used to implement the force fields in this study [eq. (2), (3), and (4)]

Dihedral Potential Parameters				
Dihedral	C₀ (kcal mol⁻¹)	C₁	C₂	C₃
CH ₃ -CH ₂ -CH ₂ -CH ₂	7.6481	14.5396	1.1339	-23.3216
CH ₂ -CH ₂ -CH ₂ -CH ₂	7.6481	14.5396	1.1339	-23.3216
CH ₂ -CH-CH ₂ -CH ₂	7.6481	14.5396	1.1339	-23.3216
CH ₂ -CH ₂ -C-C	20.0840	0.0000	-20.0840	0.0000
CH ₂ -CH-C-C	20.0840	0.0000	-20.0840	0.0000
CH ₂ -C-C-H	20.0840	0.0000	-20.0840	0.0000
CH-C-C-H	20.0840	0.0000	-20.0840	0.0000
C-C-C-C	25.9400	0.0000	-25.9400	0.0000
C-C-C-H	35.1460	0.0000	-35.1460	0.0000
C-C-C-S	35.1460	0.0000	-35.1460	0.0000
H-C-C-H	35.1460	0.0000	-35.1460	0.0000
H-C-C-S	35.1460	0.0000	-35.1460	0.0000
C-C-S-O	8.3680	0.0000	-8.3680	0.0000

3.3 Algorithms

For all simulated systems, one SWNT was maintained at the center of the simulation box of dimensions $10 \times 10 \times 7.44 \text{ nm}^3$. The cylindrical axis of the SWNT was aligned along the Z direction of the simulation box. The nanotube was not allowed to move during the simulations. To construct the initial configuration, the desired number of surfactants was placed around the SWNT with their tails perpendicular to the nanotube axis. The number of water molecules in the box was adjusted to reproduce bulk water density at ambient conditions. Periodic boundary conditions were applied in X, Y, and Z dimensions.

Before initiating the MD simulations, an energy minimization was performed to relax the system. It is known that the results of MD simulations,

particularly those for systems with slow relaxation times, can depend on their initial configurations. To minimize these effects, all systems were simulated at 1000 K for 1 ns and then instantaneously brought to 300 K. The system configurations before and after increasing the temperature to 1000 K are shown in Figure 3.2.

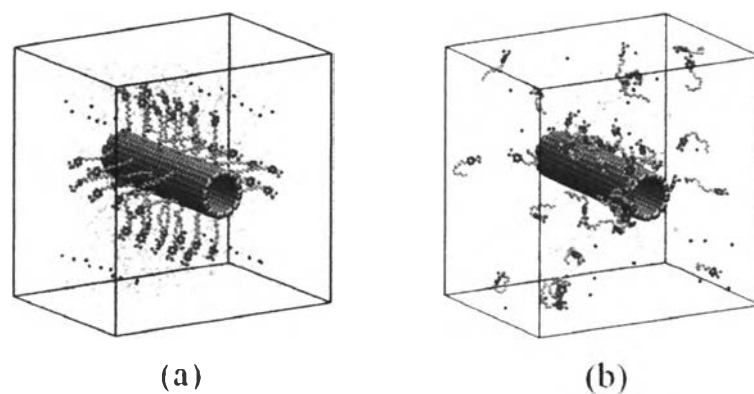


Figure 3.2 The system configuration snapshots of SDBS molecules surround the SWNT (a) before and (b) after increasing temperature to 1000 K, respectively. Color code: cyan for CH_n -groups; purple for carbon atoms in benzene rings; white for hydrogen atoms in benzene rings; red for oxygen atoms; yellow for sulfur atoms; blue for sodium counterions; grey for carbon atoms in SWNTs.

The simulations were carried out using the GROMACS simulations package, version 4.0.7 (Hess *et al.*, 2008). The equations of motion were integrated with a time step of 0.002 ps using the leap-frog algorithm (Frenkel and Smit, 1996). The simulations were conducted within the canonical ensemble in which the number of particles (N), the box volume (V), and the temperature (T) were kept constant. All simulations were carried out at 300 K using the Nose-Hoover thermostat with a relaxation time constant of 0.1 ps (Frenkel and Smit, 1996; Hoover, 1985). The long range electrostatic interactions were handled with the Particle Mesh Ewald method with a precision 10^{-4} .⁴⁴ The van der Waals interactions were treated with cut off at 9 Å. The trajectories and velocities were saved every 1000 steps (2 ps) for subsequent analysis. At low surface coverage, each system was equilibrated for 250 ns. In the case of high surface coverage, the systems were equilibrated for 400 ns (53 linear

SDBS on (6,6) SWNT; 106 branched SDBS on (12,12) SWNT; 178 branched SDBS on (20,20) SWNT) and 500 ns (106 linear SDBS on (12,12) SWNT; 178 linear SDBS on (20,20) SWNT; 53 branched SDBS on (6,6) SWNT). The last 50 and 100 ns were used for data analysis at low and high surface coverages, respectively. All simulated systems were considered equilibrated when the results did not change during the last 100 ns of simulation. The simulated systems, including the SWNTs, the total numbers of SDBS and water molecules, surfactant coverages, and the simulation times are reported in Table 3.2.

Table 3.2 Simulation details for the various systems considered

System	SWNT	Number of SDBS molecules	Number of water molecules	SDBS surface coverage (nm ² /headgroup)	Simulation time (ns)
Linear SDBS	(6,6)	19	24145	1.0	250
	(12,12)	38	23188	1.0	250
	(20,20)	63	21460	1.0	250
	(6,6)	53	23427	0.357	400
	(12,12)	106	21711	0.357	500
	(20,20)	178	18953	0.357	500
Branched SDBS	(6,6)	19	24107	1.0	250
	(12,12)	38	23172	1.0	250
	(20,20)	63	21468	1.0	250
	(6,6)	53	23418	0.357	500
	(12,12)	106	21684	0.357	400
	(20,20)	178	19022	0.357	400