Dynamic Adsorption Behavior of Surfactants on Single-Wall Carbon Nanotubes in Aqueous Media by Experimentation and Molecular Dynamics Simulation

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Abstract

The adsorption behavior of surfactant molecules on the hydrophobic surface of single-wall carbon nanotubes (SWNTs) was examined experimentally by measurement of turbidity degree and average size of dispersed SWNTs aggregate, and the molecular dynamics (MD) techniques. Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were used as model surfactants in aqueous media. The dispersion of SWNTs was investigated by MD simulation using the adsorption model of the surfactant on the SWNT surface. As a result, we found the clear difference of the adsorption behavior according to the kind of surfactants. The hydrophilic head group of SDS molecule adsorbed on the hydrophobic surface at the initial step of adsorption and the hydrophobic moiety of SDS repeated the adsorption and desorption on the surface. In contrast, the CTAB molecule formed the stable adsorption state on the hydrophobic surface. This adsorption behavior of surfactant molecule on the SWNTs surface affects the dispersion of SWNTs in aqueous media.

Key-words: Single-wall carbon nanotube, Surfactant, Sodium dodecyl sulfate, Cetyltrimethylammonium bromide, Molecular dynamics simulation

1. Introduction

Carbon nanotubes (CNTs) possess important properties derived from a combination of unique dimensional, structural and topological features. CNTs have become a focus in chemistry, physics and material science due to superior mechanical, electrical and thermal properties. However, the aggregation of CNTs is easily progressed by the van der Waals force on CNT surface. Therefore, the function for CNTs decreased by aggregation of tubes. A variety of dispersion methods have been researched. Especially, surfactant-assisted dispersion of CNTs was used with an ultrasonication. The dispersion of CNTs with some kinds of surfactants has been reported. The clarification of the adsorptive behavior of the surfactant on the CNT surface is necessary for the selection of optimum surfactant.

In this short article, single-wall carbon nanotubes (SWNTs) were used as a model dispersion of CNTs. SWNTs were dispersed by the ultrasonic irradiation in aqueous surfactant solution. The adsorptive behavior to the surface of SWNT of the surface-active agent at this time was examined from the experimental data and the molecular kinetic computer simulation. The difference between dynamic adsorption behaviors of different surfactant molecules on the SWNTs surface was discussed from the results of experimental and computational investigation.

2. Materials and Methods

Ground single-wall carbon nanotubes (SWNTs) were provided by Nikkiso Co., Ltd. Sodium dodecyl sulfate (SDS; CMC 8 mM) and cetyltrimethylammonium bromide (CTAB; CMC 0.92 mM) were used as model surfactant. The surfactant solution used the concentration around the critical micelle concentration (4.0, 8.0 and 16 mM for SDS and 0.1, 0.5 and 1.0 mM for CTAB). In advance, the entwined SWNTs fiber was roughly untied with an Alex 1505 sonication bath (40-kHz frequency; 150 Watt power) by 60-min irradiation. Aqueous surfactant solution (50 mL) containing SWNT powders (0.2 mg) were dispersed with a US-300T homogenizer Nihonseiki Kaisha Ltd., Japan (20-kHz; 300 W).

The turbidity degree of SWNTs in the aqueous surfactant solution was measured by the temporal changed of UV-absorbance intensity at 262-nm with an Agilent Technologies 8453 UV-vis spectrometer. The interval for measurement of UV-absorbance after the ultrasonic irradiation was strictly fixed. The size distribution of SWNTs was analyzed using dynamic light scattering (DLS) technique with a Nicomp 380 ZLS (Particle Sizing Systems Co.). The solutions were allowed to stand for 30 min before DLS measurement and the DLS measurement was continued for...
30 min in the interests of accuracy.

The initial adsorption behaviors of the SDS and CTAB surfactants on the hydrophobic SWNT surface in aqueous media were simulated by a molecular dynamics method. An united-atom type model for surfactant molecule (SDS or CTAB) and 1049 TIP4P type models for water molecules were packed in a rectangular simulation box with dimensions 2.65 nm × 2.65 nm × 4.54 nm (x × y × z) and periodic boundary conditions in the x and y directions. The intermolecular interaction between the water and surfactant molecules is modeled using Lennard-Jones (LJ) and coulomb potentials. The interaction potential \( \phi \) between an admolecule and a graphite surface was defined as equation (1). Here, \( z \) is the separation distance between the molecules and graphite surface and \( \varepsilon_{sf} \) and \( \sigma_{sf} \) are the energy and size parameters in the LJ potential between these molecules and a carbon atom existing in graphite sheet calculated by the Lorentz-Berthelot rule. And \( \rho_s \) is the atomic density of a graphene sheet and \( \Delta \) is the interlayer distance of graphite sheets. The movement of surfactant molecule was calculated using Leapfrog algorithms with a time step of \( 1 \times 10^{-16} \) sec.

\[
\phi = 2\pi \rho_s \sigma_{sf}^3 \left[ \left( \frac{\sigma_{sf}}{z} \right)^6 - \left( \frac{\sigma_{sf}}{z} \right)^2 \right] - \frac{\sigma_{sf}^6}{3\Delta(0.01\Delta + z)^3} \quad (1)
\]

3. Results and Discussion

The UV-visible absorbance of CTAB solution including SWNTs is shown in Fig. 1. The characteristic absorption band rooted in the \( \pi \) electron of the SWNTs appeared at 262 nm. Note that the increase in the absorbance of 262 nm was matched by the turbidity degree of SWNTs in the aqueous solution. The temporal change of turbidity degree of SWNTs according to the UV-absorbance increase against irradiation of homogenization is shown in Fig. 2. The turbidity degree depends on the amount of SWNTs dispersed in solution. This result indicates that the amount of SWNTs sustained in surfactant solution increases with the ultrasonic irradiation.

In the case of high concentration of surfactants such as SDS (8 and 16 mM) and CTAB (0.5 and 1.0 mM), the dispersion of SWNT aggregation progresses by the initial irradiation of ultrasonic wave with homogenizer. However a remarkable increase in dispersion rate does not result from by the further irradiation. On the contrary, a rapid dispersion was not observed at the lower concentration of surfactant (SDS: 4 mM and CTAB: 0.1 mM).

The average aggregate size of SWNTs was analyzed by the dynamic light scattering technique (see Table 1). In the case of SDS, the aggregated SWNTs of 134 nm were observed by the homogenization at 10-min. The average size of SWNTs aggregate decreased by 44 % and 69 % as the result of irradiation of 20 min and 30 min respectively. On the other hand, the aggregated SWNTs of 288 nm were shown with the

![Fig. 1](image1.png) The irradiation time dependence of UV-visible absorbance of the SWNTs suspension in the 1 mM CTAB solution. Here, the times shown in figure are ultrasonic irradiation time using homogenizer.

![Fig. 2](image2.png) Temporal change for UV-absorption (\( \lambda = 262 \) nm) of aqueous SWNTs suspension with (a) SDS and (b) CTAB surfactants.

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<th>Table 1</th>
<th>Change of size distribution of SWNT aggregate in aqueous SDS and CTAB dispersion.</th>
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<tr>
<td>Diameter (nm)</td>
<td>Sonication (min)</td>
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<tr>
<td>10</td>
<td></td>
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CTAB surfactant by the 10 min irradiation. The initial dispersion of aggregated SWNTs with CTAB was larger than that with SDS. The aggregation size decreased by 64% for 20 min irradiation and 70% for 30 min irradiation. The average size of dispersed SWNTs in SDS solution was smaller than that in CTAB solution. On the other hand, the turbidity ratio of SWNTs with SDS was lower than that of CTAB. These results suggest that the size boundary of SWNTs aggregate which is able to disperse in CTAB solution is larger than that in SDS solution. In other words, the large aggregate of SWNTs cannot be dispersed in the SDS solution. The difference of SWNTs dispersion is rooted in the adsorption state of surfactant molecules on the surface. These adsorption structures of SDS and CTAB molecules on the hydrophobic surface are discussed below using molecular dynamics techniques.

The initial adsorption behaviors of the surfactant molecules (SDS and CTAB) and SWNT surface in aqueous media are depicted in the cartoons of Fig. 3. The initial distance of hydrophobic group of SDS and CTAB from the SWNT surface was arranged to 1.2 nm and 0.8 nm in the simulation with 1049 water molecules displayed in the 0 sec part of Fig. 3. To facilitate visualization as to how the surfactants approach the SWNT surface, the water molecules were excluded from the rest of Fig. 3. The adsorption behavior of SDS and CTAB molecules was clearly different on the SWNT surface. The hydrophobic group (-CH₃) of CTAB had mostly approached the SWNT surface in 7 ps. Rapid adsorption after that does not progress though the hydrophilic group (-N+(CH₃)₃) of CTAB approached to a distance of 2 nm at 3 ps. The affinity of SDS/SWNT to water molecules has not dramatically increased because both the hydrophilic group and hydrophobic group of SDS were adsorbed on the SWNT surface. Therefore, the turbidity of SDS was lower than that of CTAB. In contrast with SDS, the hydrophilic group of CTAB selectively approached the SWNT surface. The hydrophilic SWNT surface was formed by the free hydrophilic head group of CTAB surfactant. Consequently, the stability dispersion of SWNT was enhanced in aqueous solution of CTAB.

Generally, the hydrogen bond of water molecules forms strongly on the hydrophilic SWNT surface. The water molecules form a strong network on the hydrophobic SWNT surface. Therefore, the surfactant molecules must destroy the network structure of water molecules when the surfactant molecule was rapidly adsorbed on the hydrophobic SWNT surface at 3 ps (1 ps = 1 × 10⁻¹² sec), the distance between hydrophilic group and SWNT surface was about 0.5 nm. On the other hand, the hydrophobic moiety (-CH₃) of SDS was desorbed in the initial step. And then, it repeated the adsorption and desorption on the SWNT surface. The affinity of SDS/SWNT to water molecules has not dramatically increased because both the hydrophilic group and hydrophobic group of SDS were adsorbed on the SWNT surface. Therefore, the turbidity of SDS was lower than that of CTAB. In contrast with SDS, the hydrophilic group of CTAB selectively approached the SWNT surface. The hydrophilic SWNT surface was formed by the free hydrophilic head group of CTAB surfactant. Consequently, the stability dispersion of SWNT was enhanced in aqueous solution of CTAB.

Fig. 3 Snap shots of adsorption behavior of SDS (a) and CTAB (b) on hydrophobic graphite surface.

Fig. 4 Separation distance between surfactant molecules and graphite surface depending on time.
approaches to the SWNT surface. The hydrophobic group (-CH₃) of SDS approached to the SWNT surface by hydrophobic effect. However, it is prevented by the water molecule on the SWNT surface. On the other hand, the hydrophilic group will easily approach to the water molecule formed on the SWNT surface because of the affinity to water molecules. The adsorption of hydrophobic moiety of SDS molecule on the graphite surface was intercepted by water molecules forming strong network on the surface because the hydrophobic moiety has not sufficient hydrophobicity to adsorb on the hydrophobic surface. In contrast with SDS, the ionic valency of hydrophilic head group of CTAB is remarkably lower than that of SDS. This difference affected the dispersion of SWNTs, which cannot be adsorbed due to the strong network of water molecules on the hydrophobic surface.

As above, the dynamic adsorption behavior of SDS and CTAB molecules on the hydrophobic surface is clearly different. This difference affected the dispersion of SWNTs which have a hydrophobic surface. The CTAB molecules can form a solid adsorption layer on the SWNTs surface. This adsorption layer can strongly avoid the aggregation of SWNTs in water phase during ultrasonic irradiation. Moreover, a stable dispersion state is maintained by the adsorption layer of CTAB. In contrast with CTAB, the SDS molecules are not forming an obvious adsorption layer on the SWNTs surface because the SDS molecules repeated the adsorption and desorption on the surface. For this reason, the SWNTs rapidly repeated the dispersion and aggregation in SDS solution during the ultrasonication. Eventually, the large aggregate of SWNTs was easily precipitated owing to aggregation of SWNTs. It is concluded that dynamic adsorption behaviors of SDS and CTAB molecules have an influence on the dispersion behavior of SWNTs.

4. Conclusion

The adsorption model of the surfactants on the hydrophobic SWNT surface has previously assumed a thorough adsorption by the hydrophobic group of surfactant. However, it was clarified to differ according to the kind of surfactants. The balance of the hydrophilic and hydrophobic groups in surfactant molecule is the important factor for the selection of the optimum surfactant to maintain the dispersion of CNTs which are a kind of hydrophobic particles.

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References