

Dispersion of Single Walled Carbon Nanotubes by Sodium Dodecyl Sulfonate Surfactants in Aqueous Solution: Molecular Dynamics Simulations

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INTRODUCTION

Diagrams showing Single Walled Carbon Nanotubes (SWCNTs), stabilized in water by sodium dodecyl sulfonate (SDS) surfactants, traditionally depict the surfactants radiating normal to the walls completely encapsulated the SWCNTs and forming spherical, semi-spherical, or cylindrical micellar structures. Despite their appealing symmetry and their intuitive structure, these traditionally-proposed surfactant formations are not validated by experimental or computational insights.^{1,2,3} Such brush-like micelles of surfactants – which have surfactant head groups shielding the organic tail of the surfactant and the nanotubes from interacting with water – are not always accurate: Although they may be a good approximation for these systems at low SWCNT separations, they seem to fail when SWCNT are well-dispersed in water³.

We use atomistic molecular dynamics simulations to investigate the nature of the interactions between SWCNTs and SDS in an aqueous media to arrive at a more complete understanding of the structure and properties of SWCNT dispersed or partially-dispersed in aqueous solutions.

SIMULATION METHODOLOGY

Classical atomistic molecular dynamics simulations are used to elucidate the relative structure, interactions and stability of sodium dodecyl sulfonate (SDS) in a periodic cell containing an 10,10 SWCNT and water. The ensemble is constructed by fixing a single SWCNT in a simulation box and randomly filling the box with SDS and water. Nothing was allowed to enter the SWCNT. The ratio of SWCNT: SDS was kept constant while the box size was varied, effectively changing the SWCNT and SDS concentrations. Each system has a net charge of zero, with initial charges determined by forcefield assignments. Three forcefields were used and compared for slight differences due to parameterization of the sulfonate head group in the surfactant. The GroMaCS forcefield⁴ was used for most of the production simulations, and the PCFF and CVFF forcefields were also evaluated for comparison. Simulations were carried out in Gromacs⁴ (equilibration and subsequent NVT simulations of 10ns in various simulation-box sizes, containing a single SWCNT of infinite length, as defined through periodic boundary conditions) or in LAMMPS⁵ (for the PCFF and CVFF forcefield assignments, for at least 10 nanoseconds of NPT simulation after system the equilibration, with two SWCNTs in each box) at ambient temperature and pressure.

RESULTS AND DISCUSSION

Insight into the molecular mechanisms of dispersion and design principles for nanocomposites can be gained from molecular modeling approaches. Figure 1 shows multiple periodic images of an example structure after 10 nanoseconds of NPT simulations for a simulation cell containing two independent SWCNTs with a separation distance of 4.89 nm from center to center. The left part of Figure 1 shows the fuzzy interface region of the surfactants as they lie down on the tubes along the tube axis. The right part of the figure shows a view normal to the tube axis with over 2 periodic images of the tubes shown and with part of the tube exposed for the purpose of visualization.

Through varying the distance between the SWCNTs by adjusting the amount of water in the system, the concentration of the SDS molecules also varied from below the critical micelle concentration (CMC) to well above the CMC (assuming pure water and SDS at ambient conditions). The structure that the SDS molecules adapt is shown to be heavily dependent on the spacing between the nanotubes, and not so much a function of the actual amount of the SDS present. Increasing the SDS concentration does thicken the fuzzy interface between the tubes and water, but has not led to the micellar structures previously reported¹.

In concert with the above findings, similar SDS structures around the nanotubes were observed in those systems where only one SWCNT per box was simulated (with a fixed SWCNT:SDS ratio and a varied simulation-box size, which defines the SDS and SWCNT concentrations in solution at NVT). Specifically, there was observed a distorted spherical micelle SDS formation, with the SWCNT residing in the center of the micelle, only for one characteristic nanotube center-to-center separation of ca. 4nm, for which the micelles between neighboring nanotubes interact most favorably. For smaller or slightly larger (e.g. 5nm) separations than this characteristic inter-nanotube separation, a disordered SDS layer was formed on top of the nanotube, in agreement with recent neutron scattering (SANS) data.³ These results strongly suggest that the disordered SDS formations around the nanotube are energetically favored in comparison with spherical/cylindrical micellar structures, unless such micelles are stabilized through micelle-micelle interactions between neighboring nanotubes. These latter micelle-micelle interactions occur around a characteristic nanotube separation, which is determined by the length of the surfactant and the number of surfactants per micelle.

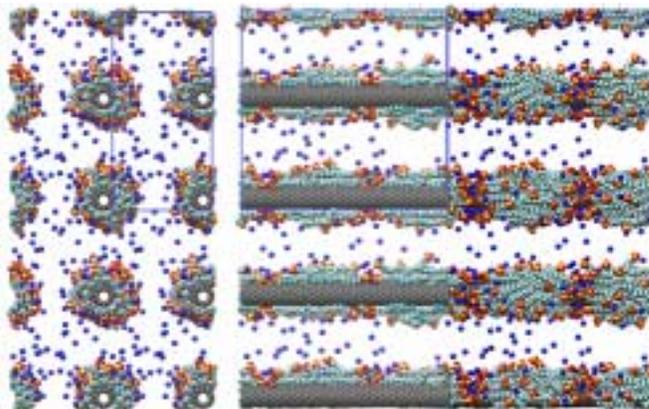


Figure 1. Example final structure of SDS surrounding a 10,10 SWCNT. The water is not shown for clarity, the blue balls are the Na⁺ cations.

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