

Small-Angle Neutron Scattering from Surfactant-Assisted Aqueous Dispersions of Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) have an array of extraordinary mechanical, thermal, and electrical properties, making them extremely desirable for a wide range of potential applications,¹ including polymer nanocomposites.² However, one impediment for their use in such applications is their affinity for one another, making it difficult to disperse them as individual tubes.^{3,4} Two routes for achieving SWNT dispersion have been suggested. The first is covalent functionalization of SWNTs.^{5,6} However, such covalent approaches have been shown to disrupt the π -networks of the SWNT, leading to possible losses in their mechanical and electrical properties.⁴ The second strategy is the use of polymers or surfactants in a solvent to assist in the dispersion of SWNTs.^{6–8} Although it has been shown that this results in an improved dispersion, the mechanism has not been unambiguously determined. In the case of surfactants, it has been previously postulated that the SWNTs form the core of cylindrical micelles of surfactants (Figure 1a)^{8–10} or are coated by adsorbed hemimicellar surfactants (Figure 1b).^{11,12} Hemimicellar adsorption of surfactants on the high-curvature surfaces of SWNTs is sterically and energetically unfavorable as suggested by Resasco et al.¹⁰ and not considered in this communication. We present structural data that refute the formation of cylindrical micelles in aqueous dispersions of sodium dodecyl sulfate (SDS)–SWNT and suggest that structureless random adsorption with no preferential arrangement of the head and tail of the surfactants is responsible for the stabilization of the dispersions (Figure 1c).

We examine SWNTs prepared by the high-pressure CO process (HiPCO)¹³ and dispersed in D₂O with sodium dodecyl sulfate (SDS). The dispersion was characterized by UV–vis absorption spectroscopy and the arrangement of the surfactant molecules by small-angle neutron scattering (SANS, performed at NIST, Gaithersburg, MD). For all samples, the UV–vis spectra exhibited the sharp van Hove transitions anticipated from individualized nanotubes. The SWNT concentration increased with SDS amount, up to 1 wt % SDS where it is 25 mg/L.¹² From UV–vis spectra we calculate that the SWNT concentrations are 7, 9, and 12 mg/L for the 0.1, 0.25, and 0.5 wt % SDS dispersions, respectively.

SANS exploits the large difference in scattering length between SDS and D₂O. The scattering length densities for SDS, SWNT, and D₂O are 4.78×10^{-7} , 7.50×10^{-6} , and $6.37 \times 10^{-6} \text{ \AA}^{-2}$, respectively. The SANS data for samples with 0.1, 0.25, 0.5, and 1 wt % SDS with and without nanotubes are shown in Figure 2. Aside from differences in the low- q scattering ($q < 0.03 \text{ \AA}^{-1}$; $q = 4\pi/\lambda \sin(\theta/2)$, λ is the wavelength and θ is the scattering angle), the data for the 0.1, 0.5, and 1 wt % samples are virtually identical with and without the nanotubes. The upturn in scattering for $q < 0.03 \text{ \AA}^{-1}$ in the SWNT dispersions is attributed to the dispersed nanotubes (Supporting Information). The contribution of this scattering to the intermediate- q behavior is insignificant ($<10^{-2} \text{ cm}^{-1}$ for $q > 0.03 \text{ \AA}^{-1}$) and not considered further in this report.

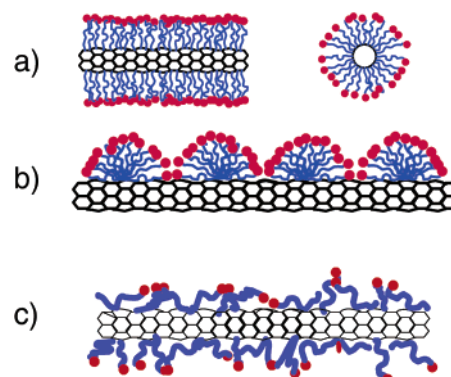


Figure 1. Schematic representations of the mechanisms by which surfactants help disperse SWNTs. (a) SWNT encapsulated in a cylindrical surfactant micelle: right: cross section; left: side view.⁸ (b) Hemimicellar adsorption of surfactant molecules on a SWNT.¹¹ (c) Random adsorption of surfactant molecules on a SWNT.

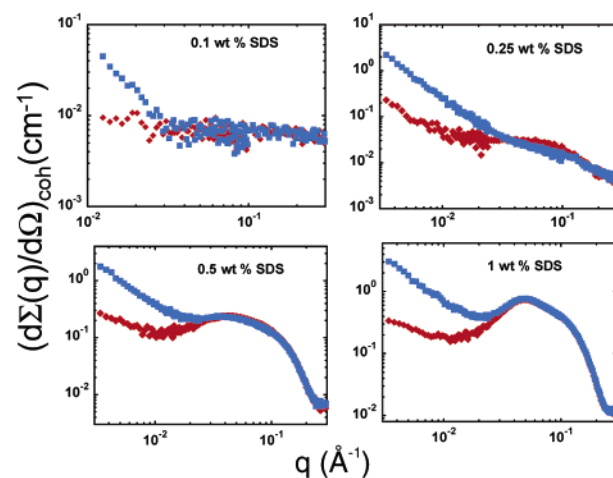


Figure 2. Coherent SANS intensities from D₂O solutions of 0.1, 0.25, 0.5, and 1 wt % SDS with (blue squares) and without (red diamonds) SWNTs at 25 °C.

For the 0.5 and 1 wt % SDS samples, the scattering from the spherical micelles is essentially unaffected both qualitatively and quantitatively and indicates little perturbation to the spherical micelles of SDS by the SWNTs. The SANS data were fit to a monodisperse micellar model with the interparticle structure based on the Percus–Yevick (PY) closure for hard spheres,¹⁴ and the structural parameters are summarized in Table 1. The data suggest minimal perturbation of the spherical micelle structure.

The 0.1 wt % SDS solution is below the critical micelle concentration ($\text{cmc} \approx 0.2 \text{ wt \%}$) and the SANS data, within the resolution of the intensity scale, demonstrate the absence of a structured material. The dispersion of SWNTs ($\sim 7 \text{ mg/L}$) results in no structural features in the intermediate- q range that would be

Table 1. Percus–Yevick Model Fit Results of the SANS Data

sample	R_m (Å) ^a	R_{hs} (Å) ^b
0.5 wt % SDS	18	57
0.5 wt % SDS + SWNTs	17	59
1 wt % SDS	17	57
1 wt % SDS + SWNTs	19	53

^a Micelle radius. ^b Hard sphere (interaction) radius.

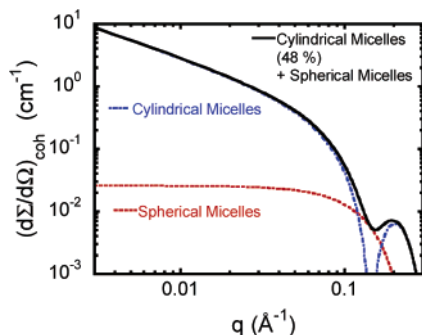


Figure 3. Coherent SANS intensities calculated for cylindrical (with an embedded nanotube) and spherical core–shell micelles at a concentration of 0.25 wt % SDS in D₂O. For both cases the calculations assume no interactions. We note excellent agreement between the experimental data and hard sphere prediction for the SDS solution. The combined cylindrical and spherical micelle prediction shown is calculated on the basis of 48% of the SDS molecules participating in cylindrical micelles.

indicative of self-assembled structures. On the other hand, the 0.25 wt % SDS solution clearly demonstrates the presence of micelles with a broad peak at $\sim 0.07 \text{ \AA}^{-1}$. Addition of nanotubes to this solution leads to a decrease in the peak intensity and the absence of any other structural development at intermediate- or high- q . On the basis of the decrease in intensity of the micellar structure peak we estimate that there is $\sim 20\%$ decrease in the spherical micelle population upon addition of SWNTs.

The SANS data for the 0.25 wt % SDS solution are adequately fitted using a simple noninteracting hard sphere model with a micellar diameter of 18 Å. For the dispersion of SWNTs we consider that the SDS molecules form noninteracting core–shell cylindrical micelles with a single nanotube acting as the core. We estimate on the basis of UV–vis spectra that the SWNT concentration in this solution is 9 mg/L. We further assume a 1.2 nm tube diameter and 200 nm length for the SWNTs¹⁵ and surfactant coverage based on the density of SDS with the shell thickness given by the SDS tail length (18 Å).¹⁶ Figure 3 shows that the scattering from a cylindrical micellar system is significantly different from spherical micelles especially at intermediate- q . Modification from rigid to wormlike cylinders and accounting of correlations of cylinders change the low- q behavior but not the intermediate- q behavior. Also shown is the expected scattering from a mixture of noninteracting cylindrical and spherical micelles, assuming the number density of cylindrical micelles is equivalent to that of SWNTs. Application of a similar cylindrical micellar model for the 0.5 and 1 wt % SWNT dispersions results in significant changes in the intermediate- q scattering and not observed in the experiments described here. Diffuse adsorption of surfactants on the nanotubes would be achieved with significantly smaller quantities of SDS as compared to cylindrical micelles and lead to a slight decrease in intensity in the intermediate- q region.

Three of the most important inconsistencies of the SANS data (at intermediate- q) with the cylindrical micelle concept are: the absence of cylindrical micelles at 0.1 wt % SDS, the absence of

intermediate- q signatures associated with cylindrical micelles for the 0.5 and 1 wt % SDS dispersions, and finally the inability of any combination of cylindrical and spherical micelles to account for the data of the 0.25 wt % SDS dispersion. On the other hand, a simple rescaling to decrease the number of spherical micelles and increase unimer (or disordered) fraction leads to an adequate fitting of the intermediate- q data for the 0.25 wt % SWNT dispersion. Additionally, the difficulty of forming stable hemi-micelles on the high-curvature nanotube surfaces has been previously outlined.¹⁰ These observations strongly suggest that the dispersion of SWNTs by SDS is due to the formation of a structureless, adsorbed layer of surfactant on the individual SWNTs (Figure 1c).

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Supporting Information Available: Experimental details, supplementary experimental evidence, data-fitting procedures, and theoretical predictions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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