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Dispersing Single-Walled Carbon Nanotubes with Surfactants: A Small Angle Neutron Scattering Study

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ABSTRACT

We have investigated the dispersion of single-walled carbon nanotubes (SWNTs) in heavy water with the surfactant octyl-phenol-ethoxylate (Triton X-100) using small angle neutron scattering. The results indicate an optimal surfactant concentration for dispersion, which we suggest results from competition between maximization of surfactant adsorption onto SWNT surfaces and a depletion interaction between SWNT bundles mediated by surfactant micelles. The latter effect drives SWNT reaggregation above a critical volume fraction of micelles. These behaviors could be general in dispersing SWNTs using amphiphilic surfactant. The data also reveal significant incoherent scattering from hydrogen in SWNTs, most likely due to acid and water residues from the purification process.

Single-walled carbon nanotubes (SWNTs) are structurally unique materials that exhibit excellent mechanical, electrical, thermal, and optical properties,[1] and they offer potential promise for a number of novel applications.[2] Although much progress has been made, it is widely recognized that the bottleneck toward applications is the purity and dispersion of SWNTs. A variety of chemical functionalization[4−6] and physical methods[7−17] have been used to achieve effective dispersion. The former have been found to deteriorate the intrinsic properties of SWNTs.[18,19] Physical approaches using amphiphilic surfactants have proven capable of debundling SWNT bundles and stabilizing individual tubes while maintaining the SWNT integrity and intrinsic properties.[8,14]

A full understanding of the fundamental mechanism for dispersing carbon nanotubes with amphiphilic surfactants is still lacking. In this paper we report a systematic small angle neutron scattering (SANS) study of SWNT suspensions in D_2O using the nonionic surfactant octyl-phenol-ethoxylate (denoted Triton X-100), which has been previously demonstrated to be effective in dispersing SWNTs.[12] Most important to this study, Triton X-100 is “clean” in the SANS spectra. That is, in a wide surfactant concentration range, the dominant structure is noninteracting micelles, which can be described by a single form factor. Therefore, the scattering from SWNTs and surfactant can be easily separated, and SANS data can be analyzed quantitatively. A general picture of dispersing SWNTs with surfactants is drawn from this study, which could provide guidance for the optimal use of such surfactants for dispersing carbon nanotubes.

Single walled carbon nanotubes were synthesized through high-pressure catalytic decomposition of carbon monoxide (HiPco batch 79).[20] SWNTs were purified by soft baking followed by brief sonication in HCl, resulting in an iron impurity less than 1% by mass.[21] The Triton X-100 surfactant was obtained from Sigma-Aldrich[22] and was used as received. It has an average molecular mass of 625, density of 1.065 g/cm^3, and a critical micelle concentration (CMC) of (0.22 to 0.24) $\times 10^{-3}$ moles/liter in water at 25 °C.

Three series of solutions were prepared in this study; 0.1% and 0.01% SWNT by mass with various concentrations of Triton X-100 surfactant in D_2O, and Triton X-100 solutions in D_2O at various concentrations. SWNT/surfactant suspensions were ultrasonicated for 24 h before SANS measurements, performed at the NIST Center for Neutron Research. With the NG1 8m SANS instrument, incident neutrons of wavelength $\lambda = 10$ Å and a sample-to-detector distance of 3.84 m yielded a range of scattering wavevector, 0.006 Å^{-1} $< Q <$ 0.1 Å^{-1}. With the NG7 30m SANS instrument, three different instrumental configurations yielded a wide Q-range of 0.0008 Å^{-1} to 0.7 Å^{-1}. The scattered neutrons were counted with a 2D detector. After correction for background

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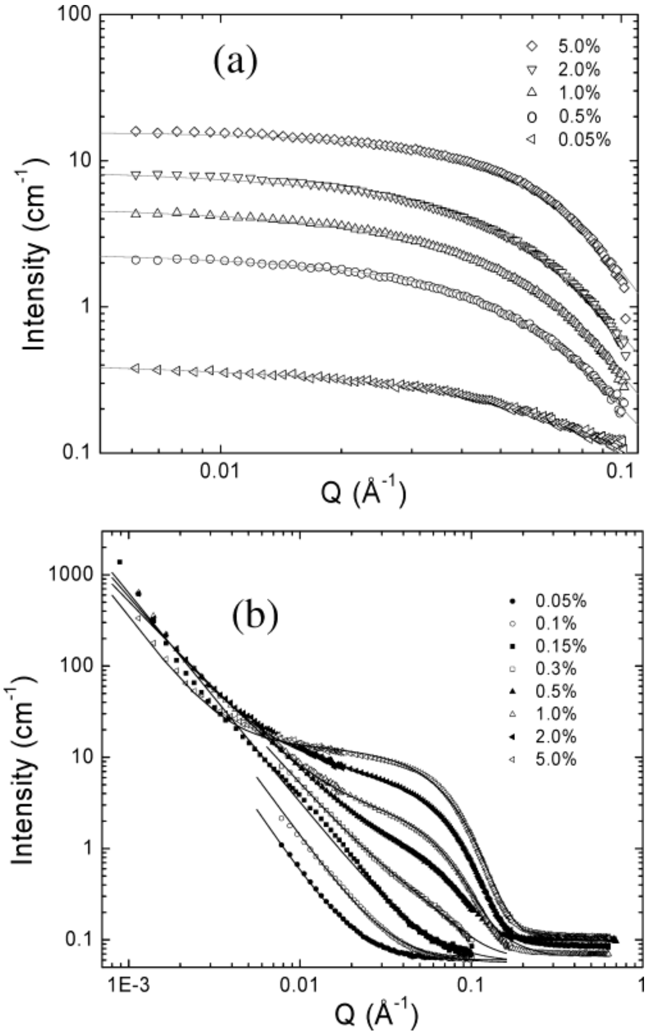

Figure 1. (a) SANS spectra of the Triton X-100 solution of various concentrations. The solid curves through the symbols are the best fits according to a micelle model as described in the text. The average radius of micelles is ca. 30 Å and the dispersity of radius $\Delta R/R_0 \approx 0.3$. (b) SANS spectra of SWNT/surfactant suspensions with 0.1% SWNT by mass and various surfactant concentrations ranging from 0.05% to 5%. The solid curves through symbols are the best model fitting.

and detector efficiency and conversion to an absolute scale using the direct beam intensity, the 2D intensity was circularly averaged to yield the total scattering cross section. All SANS measurements were carried out at 22 °C.

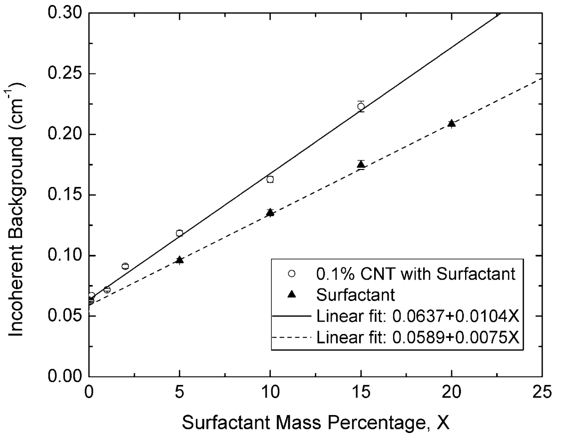

Figure 2. Incoherent background as a function of the surfactant concentration in the solution for both the 0.1% SWNT suspension (circles) and surfactant solutions (triangles). The error bars represent the finite counting statistics. The solid and dashed lines are weighted linear fits. They have different intercepts with the vertical axis.

Selected SANS spectra of the surfactant solutions and the 0.1% SWNT suspensions are shown in Figure 1. Early studies on Triton X-100 indicated that micelles are oblate ellipsoidal shaped.[23,24] In this study, micelles in the surfactant solutions can be best described by a spherical micelle model, shown as the solid curves through symbols in Figure 1a. The effect of polydispersity in radius on the overall scattering intensity could be accounted for using the Schultz distribution function.[25] Fitting SANS spectra of surfactant solutions gives an average radius of micelles $R_0 = (30 \pm 1)$ Å, and dispersity $\Delta R/R_0 \approx 0.3$. Further, the spectra for surfactant concentrations up to 5% are free of micellar correlation and are analyzed using form factors only. The micellar volume fraction, ϕ_{mi}, is found to be linearly correlated with the overall surfactant concentration, $\phi_{\text{mi}} = -0.00006 + 0.00685\ X$, where X is the mass percentage of surfactant. In SWNT suspensions (Figure 1b), the low-Q scattering is due to the surfactant-dispersed SWNTs, which shows power-law dependence. Although surfactants adsorbed on SWNT surfaces could take various textures,[26] they mainly give contrast to the SWNT scattering, and their detailed structures are averaged to give single power-law behavior. The intermediate-Q scattering comes from residual surfactant in solution. The surfactant micelles are identical in surfactant/water solutions and in SWNT suspensions. It is clear that as the surfactant concentration increases, scattering at intermediate Q-range becomes more prominent, indicating larger surfactant micelle contributions. In view of their distinct scattering pattern, the total scattering intensity is divided into three parts; power-law SWNT scattering, residual surfactant micelle scattering, and an incoherent background,

$$\frac{d\Sigma}{d\Omega}(Q) = \left.\frac{d\Sigma}{d\Omega}\right|_{\text{SWNT}} + \left.\frac{d\Sigma}{d\Omega}\right|_{\text{Triton}} + I_{\text{inc}} = \frac{I_0}{Q^{\alpha}} + I_{\text{Triton}}(Q,\phi_{\text{micelle}}) + I_{\text{inc}} \quad (1)$$

where I_0 is the coefficient of the power law, α the power exponent, $I_{\text{Triton}}\ (Q,\phi_{\text{micelle}})$ the coherent scattering intensity of surfactant micelles, and I_{inc} the incoherent background. The solid lines through the symbols in Figure 1 are the best fits according to eq 1.

The incoherent background can be clearly identified as the flat region in SANS spectra at high Q ($Q > 0.2$ Å^{-1}). The measured incoherent cross-section (Σ_i) as a function of the surfactant concentration in solution is shown in Figure 2, in which open circles are for 0.1% SWNT suspensions and triangles for surfactant solutions. The solid and dashed lines are weighted linear fits to the 0.1% SWNT and surfactant series, respectively. The two lines have distinct intercepts with the vertical axis, (0.06369 ± 0.00014) cm^{-1} and (0.05893 ± 0.00052) cm^{-1}, respectively, indicating different total contributions from SWNTs and D_2O without the surfactant. The difference of the two intercepts, $(0.0048 \pm 0.0005)\ \mathrm{cm}^{-1}$, is then due to the Σ_i of the 0.1% SWNT. This rough estimate gives a Σ_i of $(4.8 \pm 0.5)\ \mathrm{cm}^{-1}$ for the SWNTs used in this study. In view of the negligible Σ_i of carbon, this large quantity qualitatively indicates the existence of a fair amount of H, which has a large incoherent cross section.[27] We emphasize that only the order of magnitude is important here; the quantity may be subject to larger systematic errors due to the small amount of SWNTs in sample and multiple extrapolations involved in obtaining the value.

A previous study suggested small quantities of functional groups such as −H, −OH, and −COOH[28] in SWNT samples could be rather different because processing conditions vary. It is likely that in this study SWNTs after the purification process contain a fair amount of residual water and acid, as well as other H-containing species. Heating in vacuum removes these residues but also renders the SWNT intractable for sonication and suspension. Pristine SWNTs were shown previously to exhibit amphiphobic properties,[29,30] i.e., they are "phobic" to both oil and water. A recent study suggests that affinity between purified SWNTs and surfactant is mostly hydrophobic rather than Coulombic.[11] Whether the large Σ_i of purified SWNTs is related to the hydrophobicity of those tubes needs further investigation.

An important issue in SWNT dispersion is to quantitatively measure the dynamic balance between surfactant molecules absorbed on carbon nanotubes and those remaining in solution. In the dynamic balance, surfactant molecules can exist in one of three states; individual molecules in solution, in micelles, and adsorbed to SWNT surfaces. Consequently, in a steady state, those absorbed to tubes are in equilibrium with the free surfactant molecules in solution, and the latter in equilibrium with those in micelles. The amount in micellar phase could be directly obtained from fitting the SANS data. Figure 3 shows the micellar volume fraction in 0.1% SWNT suspensions as a function of the overall surfactant concentration. The solid curve is the expected surfactant micellar volume fraction in surfactant solutions based on the linear relation obtained from the surfactant study. The comparison suggests that at a surfactant loading below 0.5%, most surfactant molecules do not exist in micelles, whereas at high concentrations the micellar volume fraction takes asymptotically the solution value. The difference between the symbols and the curve represents the amount of surfactant that is either free in solution or absorbed on SWNTs. Assuming SWNTs do not affect the dynamic equilibrium, the linear relationship for surfactant solution could be used to estimate the total amount of surfactant molecules that are not adsorbed on SWNT from the volume fraction of micelles.

With the value of the total surfactant in solution, the amount of surfactant adsorbed on SWNT surfaces could be estimated. The inset of Figure 3 plots the molar surfactant adsorption per gram of SWNT as a function of overall surfactant weight percentage in the suspension. Adsorption increases with surfactant concentration and saturates around 0.5% to 1% by mass. The saturation adsorption ratio is ca. 0.004 mol/g, which is close to the recently reported value of the coverage on SWNTs.[11] Scattered data points and large error bars at high surfactant concentrations indicate the uncertainty associated with small differences of large numbers. Further quantification of the adsorption isotherm is not possible at this point because the specific surface area of SWNTs in solution varies with dispersion.

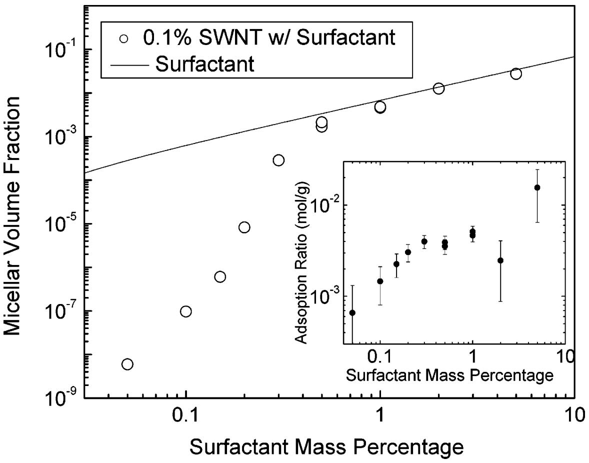

Figure 3. Micellar volume fraction in 0.1% SWNT suspensions (open circles) and surfactant solutions (solid curve) as a function of the overall surfactant concentration. Their comparison suggests that below 0.5% surfactant concentration, most surfactant molecules do not form micelles, whereas at high concentrations micellar formation dominates. The inset shows molar surfactant adsorption per gram of SWNT as a function of surfactant weight percentage in suspensions. Adsorption increases with surfactant concentration and saturates around 0.5% to 1%. The saturation adsorption ratio is ca. 0.004 moles/gram.

The SWNT scattering is characterized by power-law behavior. Individual SWNTs have diameters, D, of (1 to 2) nm and lengths, L, ranging from 100 nm to several micrometers. Theoretical predictions and mechanical measurements of the modulus of SWNTs[31,32] indicate very large persistence lengths (around 50 μm),[33] and therefore, individual defect-free SWNTs a few microns long (and less) should behave like rigid rods, which in turn display a Q^{-1} law in the Q-range $1/L < Q < 1/D$.[9] On the other hand, scattering measurements of SWNTs in suspensions and in polymer composites reveal a power law dependence with exponents, α, ranging from 2 to 3, which is attributed to branching in SWNT bundles and a wide distribution of sizes and structures.[34] Therefore α could be used for semiquantitatively assessing the degree of dispersion; the closer to 1, the better the dispersion.

Figure 4 shows α for both the 0.1% and 0.01% SWNT suspensions. α decreases with surfactant weight percentage, passes through a minimum, and then increases as the surfactant in solution becomes more concentrated. Note that the dependence on SWNT concentration is not obvious. The two data sets overlap within error, implying that the dispersion is not sensitive to SWNT concentration, at least at lower concentrations. α ranges from 1.8 to 2.8, indicating a lack of rigid rod structure dominance. This observation indicates that Triton X-100 is not as effective a surfactant for dispersing SWNTs as is NaDDBS, which gives Q^{-1}

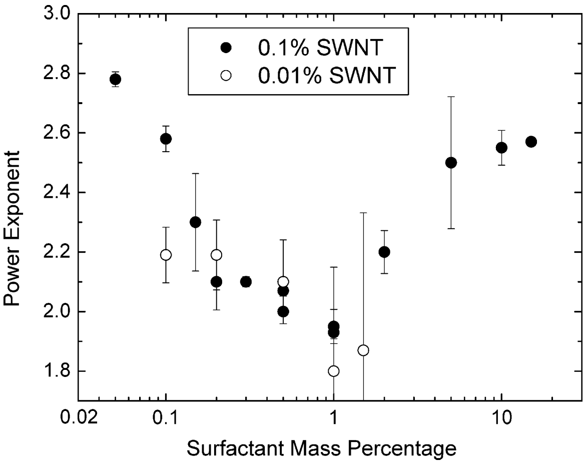

Figure 4. The power exponents for both the 0.1% and 0.01% SWNT suspensions. It is evident that the power exponent has a minimum around 0.5% to 1% surfactant concentration, indicating the optimal condition for dispersing SWNTs using Triton X-100.

power law behavior over a specific Q-range.[9] The reason could be two-fold: (1) NaDDBS is an ionic surfactant with a greater strength of hydrophobic/hydrophilic interaction, and (2) long-range Coulombic interactions among the NaDDBS molecules lead to a surfactant network that hinders Brownian motion and aggregation of SWNTs. The latter effect is apparent in the SANS spectra as a strong structure factor contribution at low NaDDBS loading and an excess scattering at low Q, which make quantitative analysis of that system rather difficult.[9]

The smallest exponent obtained in this experiment, ca. 1.9 at 0.5% to 1% surfactant concentration, implies optimal dispersion with this particular batch of SWNT using Triton X-100 surfactant. The improvement of SWNT dispersion with increasing surfactant content at low surfactant loading is intuitive. The adsorption of the surfactant onto the SWNT surface is in dynamic balance with the free surfactant in solution. As the concentration of the free surfactant increases with overall surfactant concentration, the increased chemical potential shifts the balance toward creating more SWNT surface for adsorption, resulting in better dispersion. The deterioration of the dispersion with surfactant concentration at high concentrations is somewhat unexpected. Here, we offer one possible interpretation of this observation.

At surfactant concentrations higher than 1%, most surfactant molecules reside in solution as micelles. Although still a small fraction in volume (e.g. 1% of surfactant by mass yields only 0.69% micelle volume fraction), these micelles can have a potentially large effect on the entropic interaction between SWNTs. For 3 nm radius micelles, the average micellar separation is on the order of 30 nm at a volume fraction of 0.69%, which is significantly smaller than the average length of the SWNT bundles, which varies from hundreds of nanometers to many microns, depending on the degree of dispersion. Since the much more numerous micelles have somewhat hard-wall interactions with each other and the SWNTs, the free energy of the mixture can be regarded as purely entropic and the mixture can be modeled as an ideal gas of hard spheres and long rods, with eq 1 being valid as long as spatial correlation of surfactant micelles can be neglected. At high surfactant loading, the aggregation of SWNT bundles can thus lead to a net free energy decrease associated with an increase in the free volume available to the micelles. A simple geometrical estimate suggests that the depth of such an entropic *depletion* attraction[35] between overlapping parallel straight SWNTs is of order $2k_BT$ at a surfactant loading of 1% by mass.

In summary, we have investigated the dispersion of single-walled carbon nanotubes (SWNTs) in heavy water with the surfactant Triton X-100 using primarily small angle neutron scattering. The data show that the SWNTs in this study have a large incoherent scattering cross-section, implying that they may contain residual water and acid due to the purification process. This may play an important role in the dispersion of SWNTs with amphiphilic surfactants. The data also suggest an optimal surfactant concentration for dispersion, which we suggest results from competition between maximization of surfactant adsorption onto SWNT surfaces and a micelle-mediated depletion interaction between adjacent SWNT bundles. This latter effect drives the reentrant aggregation of SWNTs above a critical micellar volume fraction, leading to the general conclusion that the amount of surfactant, rather than the surfactant/SWNT mass ratio, is the more relevant parameter in controlling dispersion. At optimal dispersion, the surfactant adsorption ratio is ca. 0.004 mol/g, comparable to previous findings. We believe the general picture revealed from this study is applicable to other surfactant systems, although the optimal concentrations of particular SWNT/surfactant pairs could be different. We hope that this study will provide insight into further understanding of the intricacies of dispersing SWNTs using amphiphilic surfactants.

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Supporting Information Available: A brief discussion of the physical understanding of the importance of entropic interactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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