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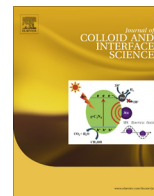
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Adsorption of sodium dodecylsulfate on single-walled carbon nanotubes characterised using small-angle neutron scattering



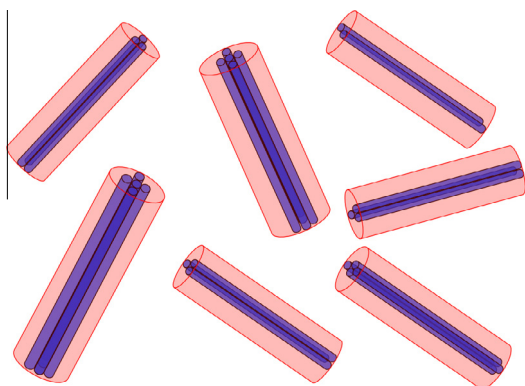
E.S. Kastrisianaki-Guyton^a, L. Chen^b, S.E. Rogers^c, T. Cosgrove^a, J.S. van Duijneveldt^{a,*}

^a School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

^b Merck Chemicals Ltd., Chilworth Technical Centre, University Parkway, Southampton SO16 7QD, UK

^c ISIS Neutron Source, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, UK

GRAPHICAL ABSTRACT



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ABSTRACT

Aqueous dispersions of single-walled carbon nanotubes are often made using sodium dodecylsulfate (SDS), which adsorbs to the nanotube surface to stabilise them. Despite SDS being commonly used with single-walled carbon nanotubes, there is no consensus on the structure of the adsorbed layer. Small-angle neutron and X-ray scattering results reported here show that the data can be fitted to a relatively simple core-shell cylinder model, consistent with a polydisperse nanotube core of radius 10 Å, surrounded by an adsorbed surfactant layer of thickness 18 Å and volume fraction of 0.5. This is consistent with small nanotube bundles surrounded by an adsorbed layer of extended SDS molecules.

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1. Introduction

Since the discovery of carbon nanotubes by Iijima they have been widely studied, due to their unique properties such as their high aspect ratio, mechanical strength and electrical conductivity [1]. Single-walled carbon nanotubes (SWCNTs) can be thought of

* Corresponding author.

E-mail address: j.s.van-duijneveldt@bristol.ac.uk (J.S. van Duijneveldt).

conceptually as a rolled-up sheet of atomically-thin carbon, with both the diameter of the resulting nanotube and the angle used when rolling up this cylinder being key parameters in determining its electronic properties. Syntheses of SWCNTs result in a third of the nanotubes being metallic, with two thirds being semiconducting [2]. There has been a surge in research interest in recent years looking into possible separation methods for these two species of nanotube in order to make SWCNTs of a single electronic type for future applications. A major challenge in utilising the properties of SWCNTs is the difficulty encountered on attempting to form a nanotube dispersion in either aqueous or organic media, due to strong van der Waals interactions between the tubes causing them to bundle together. Methods which have been investigated to overcome this problem include both covalent and non-covalent approaches, with non-covalent methods generally being favoured as they do not affect the intrinsic properties of the SWCNTs.

O'Connell et al. reported that individually dispersed SWCNTs were obtained by sonication of SWCNTs in an SDS dispersion, followed by purification by ultra-centrifugation [3]. The use of SDS has since become common to disperse and debundle SWCNTs, often with the presence of bile salts such as sodium cholate (SC) or sodium deoxycholate, with subsequent separation of metallic from semiconducting SWCNTs by ultracentrifugation. The use of ultracentrifugation suggests that surfactant-dispersed SWCNTs have different buoyancies depending on whether they are semiconducting or metallic. Molecular dynamics simulations on SDS and SC interacting with SWCNTs suggest that SDS and SC have similar binding energies when adsorbed to SWCNTs, hence suggesting that the binding energy cannot be the sole reason for their difference in buoyancy and subsequent separation when dispersed with SDS and SC [4].

Relatively few studies have looked into using small-angle neutron scattering to investigate how the surfactants adsorb onto the SWCNT surface. Yurekli et al. investigated the SANS scattering patterns from SDS-dispersed SWCNTs at very low SWCNT concentrations. By comparing the scattering observed to the predicted scattering from cylindrical micelles, they concluded that the SDS was not adsorbing in the form of cylindrical micelles. Instead, they concluded that the SDS was adsorbing in the form of a structureless layer, with the nanotubes present as individually dispersed particles rather than bundles [5].

Tummala and Striolo investigated the adsorption of SDS on SWCNTs using computational methods. It was reported that due to the high surface curvature of individual SWCNTs, SDS molecules are adsorbed onto the SWCNT surface in a flat orientation, rather than forming a micelle-like structure around the SWCNT [6]. Clar et al. investigated the interaction of SDS-decorated metallic and semiconducting (m- and s-)SWCNTs with agarose gel, which had been modified in order to study the effect of ionic, hydrophobic and π - π interactions on the retention of SWCNTs. Ion-dipole interactions between the SDS-decorated SWCNTs and the permanent dipoles of the agarose gel were identified as the key interactions influencing the separation of SWCNTs in this way. The authors proposed a model whereby the adsorbed layer of SDS on s-SWCNTs consisted of SDS molecules lying flat on the SWCNT surface, whereas SDS adsorbed on m-SWCNTs formed a cylindrical micelle-like structure [7].

This paper focusses on the analysis of small-angle scattering studies of SWCNTs dispersed with SDS in order to characterise the adsorption. It has been found that a core-shell cylinder model can be used to fit the data effectively, with a polydisperse SWCNT core giving the best fits to both the SANS and SAXS data. The data fitting is shown to be consistent with a small SWCNT bundle of radius 10 Å surrounded by an 18 Å thick adsorbed SDS layer consisting of 50% solvent and 50% SDS. Although similar experiments have been previously reported in the literature, to the best of the

authors' knowledge this is the first time such a wide range of contrasts has been studied and a model has been found that convincingly fits the data across all contrasts. This suggests that SWCNTs dispersed with SDS are present as small bundles surrounded by an extended layer of SDS.

2. Materials and methods

Single-walled carbon nanotubes (SWCNTs) synthesised by a high pressure carbon monoxide (HiPCO) method were purchased from NanoIntegris ("purified" grade). Sodium dodecylsulfate ($\geq 99\%$), sodium dodecylsulfate- d_{25} (98 atom % D), sodium cholate hydrate ($\geq 99\%$) and D_2O (99.9 atom % D) were purchased from Sigma Aldrich.

2.1. Preparation of dispersions

Sample preparation involved dissolving the surfactant in water (either hydrogenated or deuterated) overnight whilst on a roller-mixer. All samples were made by addition of the required mass of SWCNTs to 2 ml of a surfactant solution (made from stock solutions of d- or h-SDS in D_2O and H_2O) of the correct concentration, followed by sonication (QSonica Q125, 125 W) in pulsed mode at 57% max power at room temperature for 1 h. The samples were then centrifuged for 40 min at 20,800g, and the top ~ 1.5 ml of the resulting supernatant was removed for use in scattering experiments. As this was already a purified grade of SWCNTs, only this centrifuge step was used in sample preparation, in keeping with previous studies [5]. It is important to note that the SWCNT concentration of 0.4% w/w quoted is not the final concentration, but rather is the concentration calculated before purification by ultracentrifugation, and that the SWCNTs are thought to be present as a mixture of electronic types. The concentrations were subsequently compared using UV-visible spectroscopy and the SWCNT concentration was estimated to be $\sim 1/2$ of the original concentration, a relatively high amount thought to be a consequence of the high purity of SWCNTs used.

2.2. Small-angle neutron scattering

Small-angle neutron scattering experiments were performed on the SANS2D small-angle diffractometer (unless otherwise stated) at the ISIS pulsed neutron source (STFC Rutherford Appleton Laboratory, Didcot, UK). A collimation length of 4 m and an incident wavelength of 1.75–16.5 Å was used. Data were measured simultaneously on two 1 m² detectors to give a Q range of 0.0045–1.92 Å⁻¹. The small-angle detector was positioned 4 m from the sample and offset vertically 60 mm and sideways 100 mm. The wide-angle detector was positioned 2.4 m from the sample, offset sideways by 980 mm and rotated to face the sample. The beam diameter was 8 mm. Each raw scattering data set was corrected for the detector efficiencies, sample transmission and background scattering and converted to scattering cross-section data ($\delta\Sigma/\delta\Omega$ vs. Q) using instrument-specific software [8].

When explicitly stated, data were also obtained on the LOQ small-angle diffractometer at the ISIS pulsed neutron source, where data were recorded on a single two-dimensional detector to provide a Q -range of 0.009–0.283 Å⁻¹, utilising neutrons with $2 \leq \lambda \leq 10$ Å.

All data were placed on an absolute scale (cm⁻¹) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene), in accordance with established procedures [9]. Samples were studied in 2 mm or 1 mm square quartz cells depending on the D_2O/H_2O content. All samples were run at

25 °C and all data sets had background solvent scattering subtracted.

Samples contain free SDS (whose scattering is dominated by micelles) plus SDS-decorated CNTs. In addition, the amount of water in both the core and shell had to be the same across all contrasts. We did not have software that could do a simultaneous fit of a suitable model across the three SANS contrasts plus the SAXS contrast; instead we followed the approach detailed below.

The SDS micelle signal was subtracted from the data. As some of the SDS was adsorbed, only a portion of this signal could be subtracted. The amount to be subtracted was decided by scaling down the SDS data so that the scattering curves overlapped at high Q (see the supporting information for further details). The remaining scattering (from SDS-decorated SWCNTs) is plotted in Figs. 3 and 4.

This data were modelled using a core-shell cylinder model, as previously used for SWCNTs decorated with the Pluronic block copolymer F127 [10]. With SANS, length scales of up to ~ 1400 Å could be probed (calculated as $2\pi/Q_{min}$ where $Q_{min} = 0.0045$ Å $^{-1}$). The CNTs are much longer than this (see the supporting information for TEM images proving this) so no features associated with the nanotube length could be probed. Therefore the length was set to an arbitrary value of 10,000 Å.

The model parameters used are shown in Table 1. For each contrast, the scattering length densities of the core and shell were calculated from the water content and the known scattering length densities for water and carbon (details on calculating the scattering length density of SWCNTs are given in the supporting information to this paper). SasView fitting software was used to evaluate the model and χ^2 for a given set of parameters at each contrast [11]. The fitting procedure involved setting the values for the polydispersity of the thickness to a certain value, and allowing the radius of the core and the thickness of the shell to vary within a range of values thought to be physically reasonable. A few examples of the resulting fits are shown here, with several more given in the supporting information to demonstrate the sensitivity of the fit to variation of the parameters.

2.3. Small-angle X-ray scattering

Small-angle X-ray scattering experiments were done using a GANESHA 300 XL (SAXSLAB, Copenhagen, Denmark) SAXS system, with an adjustable sample detector set to 1.041 m. X rays were detected using an in-vacuum Pilatus 300k detector (Dectris, Baden, Switzerland) and were generated using a sealed tube generator with a copper anode (X-ray wavelength 1.54 Å). Fluid samples were loaded into 1.5 mm quartz-glass capillary tubes (Capillary tube supplies, UK). Measurements were performed for 10 min. A transmission-normalised surfactant background was subtracted from the data, and a mask was used to remove sections of data not related to sample scattering, such as the beamstop. The data were radially averaged to produce one-dimensional scattering

curves, which were fitted using SasView fitting software, as described in Section 2.2 [11].

2.4. UV-visible spectroscopy

UV-vis spectra were obtained using a HP/Agilent 8453 spectrophotometer over the range 400–1100 nm. Samples were diluted by a factor 30 with deionised water and run in square quartz cells with a 10 mm path length. Background water absorption was subtracted from all data.

3. Results and discussion

3.1. UV-visible spectroscopy

In order to fit the data obtained, the concentration of SWCNTs had to be estimated. The relative concentrations of SWCNT in each sample was evaluated by comparing the UV-vis absorption in each case, which were then compared to a reference SC/SWCNT dispersion (spectrum shown in the Supporting Information), whose concentration was determined as follows. The sample was diluted, transferred to dialysis tubing and submerged in deionised water. The water was changed roughly once every 24 h for two weeks, at which point the carbon in the sample had coagulated, suggesting the removal of the surfactant from the sample. The sample was dried and weighed, and the SWCNT concentration was estimated to be 0.05% w/w from the mass of SWCNTs remaining after dialysis.

It was estimated that (without dilution of the sample) every unit of absorbance at a wavelength of 400 nm corresponded to $\sim 1 \times 10^{-5}$ g ($\pm 30\%$) of carbon in the dispersion per cm 3 of sample. Due to the extremely small masses of SWCNT per sample (of order 0.1 mg), this method of weighing the dried SWCNTs has a large error associated with it. The concentration values obtained here are consistent with those reported in the literature for dispersions such as these [12].

The UV-vis spectra taken of the SWCNT dispersions stabilised with SDS showed peaks which were very similar to those seen with SWCNTs stabilised with the Pluronic block copolymer F127, and a comparison of the two spectra is made in Fig. 1. The structure of F127-stabilised SWCNT dispersions has been previously shown to consist of small bundles [10].

The UV-vis peaks from 400 to 550 nm are thought to correspond to S_{33} transitions from semiconducting nanotubes, while the region from 550 to 900 nm is thought to correspond to M_{11} transitions, from metallic tubes. Thus it is thought that both metallic and semiconducting nanotubes are present in these samples [13]. In addition, the sharpness of the peaks is indicative of the degree of bundling. If single tubes were present in the dispersion, the resulting absorbance peaks would be sharper than those seen here [14]. Therefore, it has been assumed that SWCNTs in the SDS dispersions studied here consist of thin bundles of SWCNTs with a small volume of water present in the bundles. It should be noted that the SDS/SWCNT sample whose spectrum is shown in Fig. 1 was diluted in order to allow easier comparison to the F127/SWCNT spectrum.

3.2. Small-angle scattering

Small-angle scattering experiments were performed at a range of contrasts to study the adsorption of SDS onto SWCNTs. The contrasts studied are:

1. h-SDS/SWCNTs in D $_2$ O (SANS and SAXS).
2. d-SDS/SWCNTs in 15% D $_2$ O, 85% H $_2$ O.

Table 1

Table of parameters used in Figs. 3 and 4. The χ^2 value is the summed value for the χ^2 of the four fits in each case. The core radius and shell thickness were allowed to vary slightly between fitting attempts.

Parameter	Fig. 3	Fig. 4
Water in core (%)	30	30
Water in shell (%)	50	50
Radius (Å)	5	10
Shell thickness (Å)	10	18
Polydispersity of shell thickness	0	0
Polydispersity of core radius	0.7	0.7
χ^2	243	24

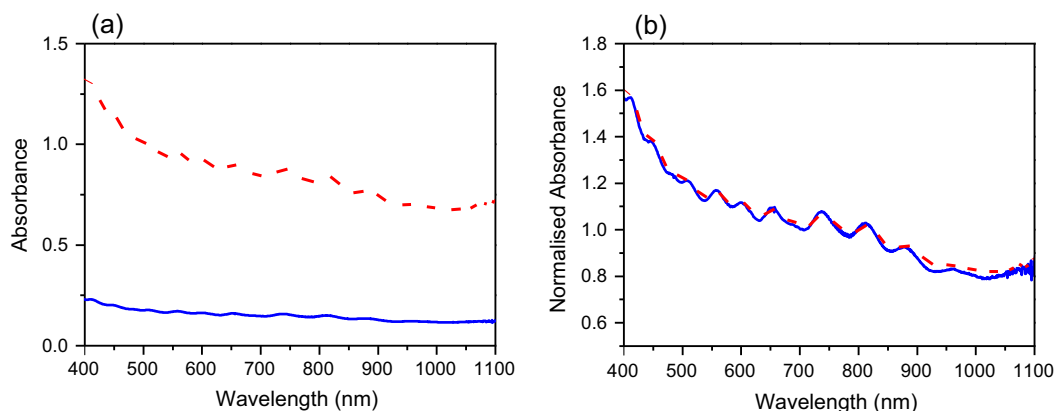


Fig. 1. UV-vis spectra of SWCNTs dispersed with F127 (red dashed lines) and SDS (blue lines). Panel (a) shows the spectra before scaling, while panel (b) shows the spectra after all absorbance values were normalised relative to the absorbance at 800 nm. It can be seen that the peaks in the normalised spectra are similar. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Contrast matched (cm-) SDS (h-SDS/d-SDS mixture) in D₂O. The scattering length densities of h- and d-SDS are below and above the scattering length density of D₂O respectively, and thus SDS can be contrast matched to D₂O ($\rho_{h-SDS} = 0.33 \times 10^{-6} \text{ \AA}^{-2}$; $\rho_{d-SDS} = 6.80 \times 10^{-6} \text{ \AA}^{-2}$; $\rho_{D2O} = 6.36 \times 10^{-6} \text{ \AA}^{-2}$).

The scattering length density profiles of the contrasts studied are shown in Fig. 2, assuming 30% water in the core and 50% water in the shell. The first contrast is SWCNTs dispersed with SDS in D₂O, where both SDS and SWCNTs are visible, and the core and shell have a positive and negative contrast to the solvent, respectively. The second is SWCNTs in 15% D₂O, where both the core and shell have a positive contrast to the solvent. Thirdly, contrast matched SDS (a mixture of h- and d-SDS) is studied with SWCNTs in D₂O, in order to obtain the scattering from the SWCNT core. All three contrasts were studied with SANS, with the h-SDS in D₂O sample also studied using SAXS. The range of contrasts studied and the inclusion of SAXS adds multiple constraints to the fitting procedure, allowing greater confidence in the resulting fits.

The scattering data for SWCNTs (0.4% w/w) dispersed with only SDS (1% w/v), after background solvent and surfactant scattering subtraction, can be seen in Figs. 3 and 4. A core-shell cylinder model was used to fit the data, which has been shown in

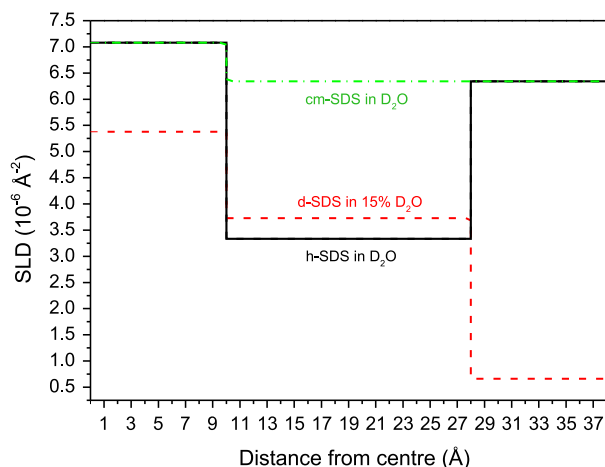


Fig. 2. Scattering length density profile for the 1% SDS/SWCNT samples studied with SANS: h-SDS in 100% D₂O, d-SDS in 15% D₂O and cm-SDS in 100% D₂O. Scattering length densities correspond to 30% water in the core and 50% water in the shell, the values obtained in the final fits (see Fig. 4).

previously published work as describing F127-decorated SWCNTs well [10]. For the fits shown in Fig. 4, it can be seen that SWCNTs dispersed with h-SDS in D₂O scatter with a lower intensity than the data for SWCNTs dispersed with d-SDS in 15% D₂O. This is a consequence of the difference in scattering length densities (based on the fit parameters used).

Fig. 3 shows attempts to fit the subtracted scattering data (with the subtractions used given in the supporting information to this paper) to a core-shell cylinder model using a core radius of 5 Å and a shell thickness of 10 Å (the full parameters are given in Table 1), as reported previously by Yurekli et al. [5]. It is clear that a good fit cannot be obtained with these parameters, and in addition the volume fraction needed to obtain a fit close to the data was a factor of ten larger than the calculated value based on absorbance measurements. The data shown in panel (a) were obtained at LOQ and a second data set obtained at SANS2D is shown in the supplementary information; data before subtracting the surfactant scattering are given in the supporting information to this paper.

Data in panels (a), (b) and (d) of Fig. 3 do not follow the curvature of the core-shell model, suggesting that the parameters used do not best describe the data. Further attempts to fit the data to a core-shell cylinder model with different parameters are shown in the supporting information to this paper.

The best fits obtained are shown in Fig. 4, where a large polydispersity (S.D./mean = 0.7) has been included for the radius of the SWCNT core, and a core radius of 10 Å and a shell thickness of 18 Å have been used. These values correspond to a small nanotube bundle surrounded by a more extended adsorbed SDS layer. The polydispersity accounts for variation in the number of CNTs per bundle; the SWCNTs are not present as individual tubes. This model is supported by TEM images in the supplementary information to this paper, which show both that the nanotubes are present as small polydisperse bundles (with the diameter of one nanotube seen to be ~1 nm), and that, upon drying, the repeat distance between bundles is consistent with the dimensions of two extended layers of SDS.

In order to test the validity of the model, the area per SDS headgroup has been calculated and compared to the area per headgroup in an SDS micelle. In this model, the area per headgroup has been calculated to be 53 Å², whereas the area of a headgroup in an SDS micelle, assuming a micelle radius of 22 Å and aggregation number of 74, is 82 Å² per headgroup. The model is thus consistent with the expected area per headgroup of a micelle, which is larger than the headgroup area obtained here due to the larger curvature of the micelle [15]. In addition, it should be stressed that the volume fraction of SDS in the adsorbed layer is 0.5, compared to between ~0.6

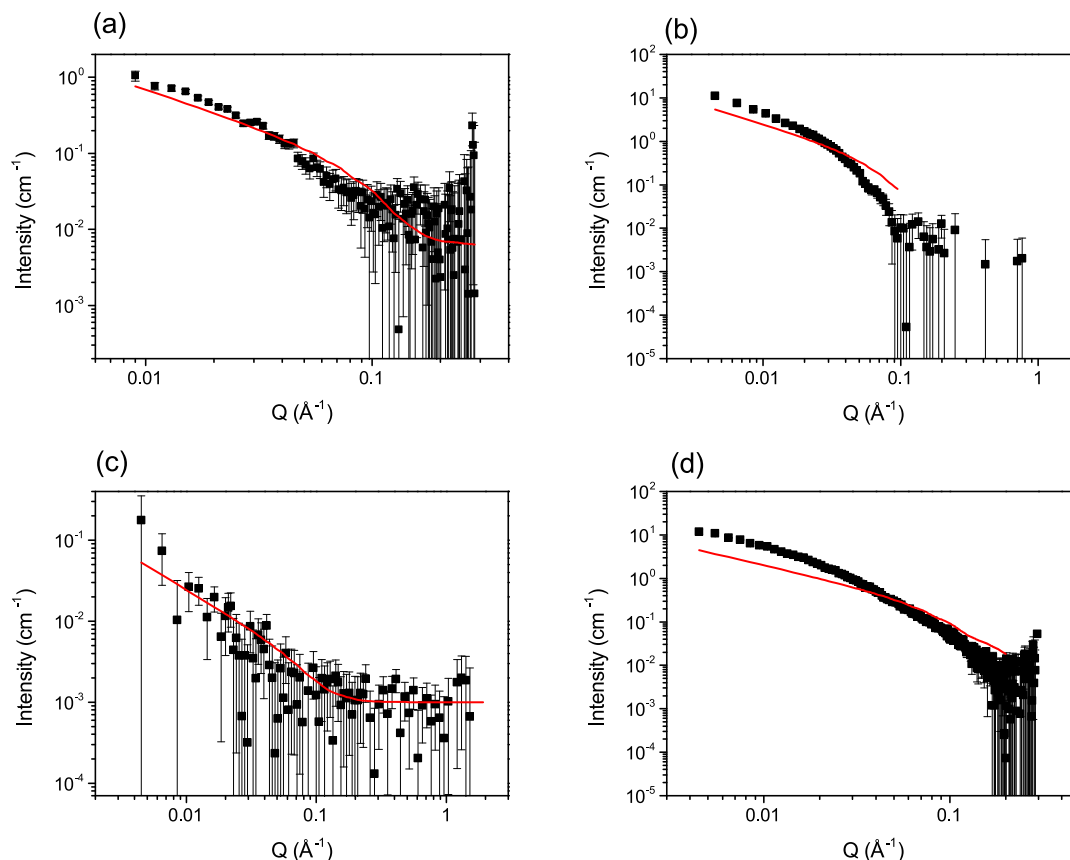


Fig. 3. Fitting 1% SDS SANS data to a core-shell cylinder model with a radius of 5 Å, polydispersity in the core size, with a 10 Å adsorbed layer thickness and a volume fraction of SDS in the adsorbed layer of 0.5. Scattering curves from: (a) h-SDS in D₂O with SWCNTs; (b) d-SDS in 15% D₂O with SWCNTs; (c) cm-SDS in D₂O with SWCNTs. (d) small-angle X-ray scattering curve of h-SDS in D₂O with SWCNTs. Volume fraction of cylinders used: (a) 0.0044; (b) 0.0044; (c) 0.0070; (d) 0.0010. Further parameters for these fits are given in Table 1.

and 0.8 in a micelle [15]. This suggests that the adsorbed layer has a higher degree of disorder than an SDS micelle.

The adsorbed amount can be calculated based on the fit parameters used, and compared to the adsorbed amount based on the subtraction of the surfactant scattering. The data shown in Fig. 4 for h-SDS/SWCNTs in D₂O only had 90% of the scattering data for 1% h-SDS in D₂O subtracted from it, thus it can be assumed that the other 10% of the surfactant had adsorbed onto the SWCNT surface, which corresponds to an adsorbed amount of 0.001 g per cm³ of dispersion. This can be compared to the adsorbed amount calculated from the fit parameters for the fit in Fig. 4(a). Using a volume fraction of cylinders of 0.0022, a volume fraction of SDS in the shell of 0.5, a core radius of 10 Å and a shell thickness of 18 Å, an adsorbed amount of 0.00095 g is obtained per cm³ of dispersion, so the fit has a good agreement to the adsorbed amount estimated from the surfactant scattering subtraction. Further scattering attempts are given in the supporting information to this paper, where it can be seen that the data cannot be fitted to a model where the SWCNTs are present as single, un-bundled tubes.

For a flat carbon surface, the concentration of SDS molecules at the carbon surface will be the same as the concentration of SDS molecules calculated at the SDS headgroup/water interface. For a highly curved surface such as that studied here, the concentration of SDS molecules will be different at the carbon surface than it will be at the interface between the SDS headgroups and the solvent. The concentration of SDS molecules at the interface between the SDS headgroups and water has been estimated by multiplying the adsorbed amount calculated at the SWCNT surface by the ratio between the radius of the SWCNT bundle (10 Å) and the radius of a

SWCNT bundle with an adsorbed SDS layer (28 Å). The adsorbed amount calculated on the SWCNT surface was calculated to be $\sim 1.8 \text{ mg m}^{-2}$, based on a core radius of 10 Å, a shell thickness of 18 Å, a value of ϕ_{SWCNT} of 0.0022, and the adsorbed amount found from the data subtraction. Using this adsorbed amount, the adsorbed amount at the headgroup/water interface was calculated to be $\sim 0.64 \text{ mg m}^{-2}$. Ma and Xia reported a maximum adsorbed amount for SDS at the carbon black-water interface of 1.3 mg m^{-2} , which is between the values obtained in this study for the adsorbed amount at the SWCNT surface and the adsorbed amount at the headgroup/water interface [16].

The fits presented show that the SANS results are consistent with small SWCNT bundles of average radius 10 Å. This agrees with the degree of bundling predicted from comparing the absorption spectra measured here with those reported previously [10]. The model is also consistent with SWCNT bundles with a large polydispersity in their radius, surrounded by an adsorbed layer of SDS of thickness 18 Å, with a volume fraction of SDS of 0.5 in the adsorbed layer. The dimensions of the adsorbed layer are consistent with extended SDS molecules, with the SWCNT bundle surrounded by an SDS monolayer. Similar to the structure of SDS micelles, the water present in the adsorbed layer is thought to be present in the headgroup region of the adsorbed layer, however the core-shell cylinder model used to fit the data assumes a homogeneous shell [15]. A core-two shell model would thus be required to ascertain whether water is present only in the headgroup region. Such a model has not been used here due to the complexity involved in fitting data across several contrasts with more variables than those used in the fitting process reported here. The Q -dependence of the

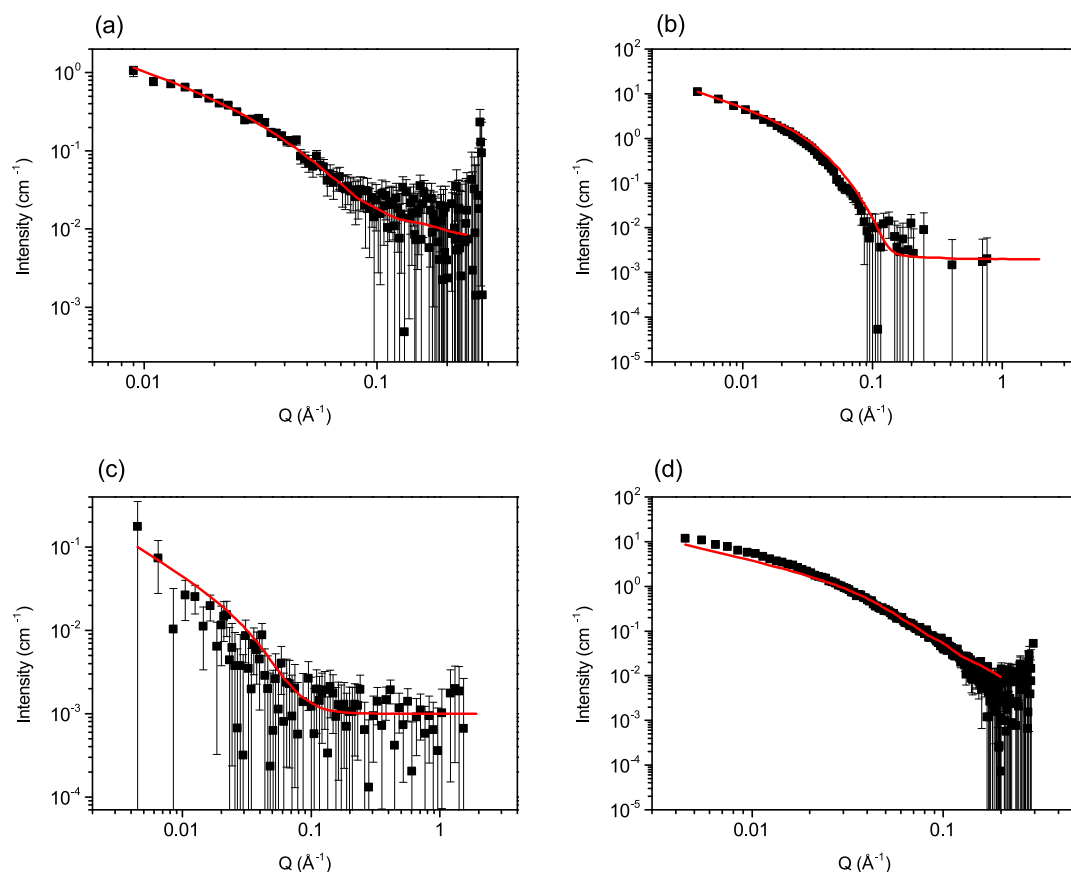


Fig. 4. Fitting 1% SDS SANS data to a core-shell cylinder model with a large polydispersity in the core radius. Fit parameters are given in Table 1 and scattering curves as described in Fig. 3. Volume fraction of cylinders based on absorption measurements: (a) 0.0022; (b) 0.0022; (c) 0.0035; (d) 0.0050.

data is related to the size of the core and the adsorbed layer, and it is therefore thought that the data cannot be fitted to a model where the SDS molecules adsorb to the SWCNT surface in a flat, disordered way.

4. Conclusions

Single-walled carbon nanotubes are commonly dispersed in water with sodium dodecylsulfate and sodium cholate, both separately and as mixtures [3,4]. Small-angle neutron scattering data for single-walled carbon nanotubes dispersed with sodium dodecylsulfate have been successfully fitted to a relatively simple core-shell cylinder model. The core is thought to consist of a small nanotube bundle rather than individually dispersed tubes. The shell consists of adsorbed surfactant chains with an average layer thickness of 18 Å and an SDS volume fraction of 0.5, similar to the dimensions of an SDS micelle. This is in contrast to previously reported reports, which suggest that SDS-dispersed nanotubes are present as single tubes surrounded by a thin and disordered SDS layer [5]. It is hoped that the fitting strategy used here could be used to analyse the adsorption of sodium dodecylsulfate and sodium cholate in mixtures, and thus to obtain more detailed information on how the two surfactants adsorb differently.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2016.03.026>. Figure source data is available at <http://dx.doi.org/10.5523/bris.1blyhopxhqxc1g3fmsktqajd>.

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