DOI: 10.1002/chem.200600326

Individual Dissolution of Single-Walled Carbon Nanotubes in Aqueous Solutions of Steroid or Sugar Compounds and Their Raman and Near-IR Spectral Properties

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Abstract: The individual solubilization of single-walled carbon nanotubes (SWNTs), achieved by using ten different anionic-, zwitterionic-, and nonionic-steroid biosurfactants and three different sugar biosurfactants, was examined. Aqueous micelles of anionic cholate analogues, such as sodium cholate (SC), sodium deoxycholate (SDC), sodium taurocholate (STC), sodium taurodeoxycholate (STDC), sodium glycocholate (SGC), as well as *N*,*N*-bis(3-D-gluconamidopropyl)cholamide (BIGCHAP) and *N*,*N*-bis(3-D-gluconamidopropyl)deoxycholamide (deoxy-BIGCHAP), exhibited good abilities to dissolve the SWNTs individually. Aqueous micelles of nonionic biosurfactants, such as sucrose monocholate (SMC), *n*-octyl-β-D-glucoside (OG), *n*-decyl-β-D-maltoside (DM), and *n*-decanoyl-*N*-methylglucamide (MEGA-10), could dissolve the SWNTs, however, the solubilization abilities were weaker than those of the anionic cholate analogues. In sharp contrast, the solubilization abilities of the zwitterionic micelles of 3-[(3-cholamidopropyl)dimethylammonio]propanesulfonic acid (CHAPS) and 3-[(3-cholamidopropyl)-dimethylammonio]-2-hydroxypropanesulfonic acid (CHAPSO) were very low, and almost zero for OG. It is evident that the chemical structures, in particular the substituent groups of the surfactants, play an important role in the solubilization of SWNTs. The near-IR photoluminescence behaviors of the SWNTs dissolved in aqueous micelles and in 1 mM biosurfactants were investigated. The chirality indices of the SWNTs dissolved in these solutions depend on the chemical structures of the biosurfactants. The Raman spectra of the SWNTs dissolved in a 1 mM solution of SC suggest the selective extraction of the metallic SWNTs. Finally, a possible solubilization mechanism using steroid surfactants is described. The SWNTs dissolved individually in water-containing biocompounds are useful in many areas of nano- and materials chemistry.

Keywords: biosurfactants · chirality · fluorescence spectroscopy · nanotubes · solubilization

Introduction

Since their initial discovery,[1] carbon nanotubes (CNTs) have been materials of interest in many fields of science and technology, due to their remarkable electronic, mechanical, and thermal properties.[2] However, CNTs themselves are insoluble in solvents, and, therefore, chemical, biochemical, and biological (medical) applications of these materials have been hindered. Our current interest is the design of CNT solubilizers as well as applications of soluble CNTs.[3,4] We have already reported that compounds carrying a polycyclic aromatic moiety, such as pyrene[5] and porphyrin,[6] act as CNT solubilizers. The combination of CNTs and biological molecules is of interest in many chemical and biochemical areas. We[7] and others[8] have reported that double-stranded and single-stranded DNA molecules dissolve single-walled carbon nanotubes (SWNTs) in aqueous solutions. CNTs are insoluble in an aqueous solution of amylose, but they are soluble in an aqueous solution of an amylose–iodine complex.[9] Schzophyllan (β-1,3-glucans) and curdlan can entrap SWNTs in their helical superstructures in aqueous solution.[10] The cyclic oligosaccharide η-cyclodextrin, composed of 12 glucosidic units, forms an inclusion complex with SWNTs like a polyrotaxane.[11] An amphiphilic α-helical peptide was designed specifically to not only coat and solubilize CNTs, but also to control the assembly of the peptide-coated CNTs into macromolecular structures through peptide–peptide interactions between adjacent peptide-wrapped CNTs.[12]

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Several types of surfactants, such as sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium bromide, and Triton X-100, are known to dissolve CNTs in water.[13] We[14] and Hertel's group[15] recently described that aqueous cholate micelles could dissolve SWNTs. A preliminary account of this study is given in reference [14]. In the present study, 13 different anionic-, zwitterionic-, and nonionic-steroid-moiety-carrying biosurfactants and three different sugar biosurfactants are used (Figure 1). All these compounds are known membrane-protein solubilizers.[16] Bile salts, such as sodium cholate and its analogues, are composed of a rigid hydrophobic steroid backbone carrying two or three hydroxy groups stereochemically, and these form specific structures and have biological functions in water.[16] Here, we describe 1) a strong chemical-structure dependence and the effect of critical micellar concentration (cmc) on the solubilization of CNTs by using the 13 biosurfactants, and 2) a possible selective discrimination of the CNT chirality index at concentrations below the cmc of the biosurfactants. The aqueous solutions of solubilized CNTs were characterized by performing visible/near-IR, near-IR fluorescence, and Raman spectroscopies. As CNTs, we used the single-walled CNTs known as HiPco.

Experimental Section

SWNTs (HiPco, the length and diameter of pristine SWNTs are ca. 1–10 mm and 0.8–1.2 nm, respectively) were purchased from Carbon Nanotechnologies and were used as received. Sodium cholate (SC), sodium deoxycholate (SDC), and sodium taurocholate (STC) were obtained from Wako Pure Chemical, Tokyo Kasei, and Acros, respectively. Sodium taurodeoxycholate (STDC) and sodium glycocholate (SGC) were purchased from Nacalai tesque. 3-[(3-Cholamidopropyl)dimethylammonio]propanesulfonic acid (CHAPS), 3-[(3-cholamidopropyl)dimethylammonio]-2-hydroxypropanesulfonic acid (CHAPSO), sucrose monocholate (SMC), *N*,*N*-bis(3-D-gluconamidopropyl)cholamide (BIGCHAP), *N*,*N*-bis(3-D-gluconamidopropyl)deoxycholamide (deoxy-BIGCHAP), *n*-octyl-β-D-glucoside (OG), *n*-decyl-β-D-maltoside (DM), and *n*-decanoyl-*N*-methylglucamide (MEGA-10) were purchased from DOJINDO Chemical. All these surfactants were used as received.

Typical procedures for the solubilization of SWNTs are as follows: About 0.5 mg of SWNTs was added to an aqueous solution (5 mL) of a biosurfactant, and the mixture was sonicated by using an ultrasonic cleaner (Branson 5510) for 1 h, followed by centrifugation at 60000 g.

UV/visible/near-IR and near-IR emission spectra were measured by using a spectrophotometer (JASCO, V-570) and a Horiba Spex Fluorolog-NIR spectrofluorometer, respectively. Raman spectra (excitation wavelength of an Ar ion laser 514.5 nm) were measured by using a Renishaw Ramanscope System 1000 for samples prepared by casting from solubilized SWNTs in water. Atomic force microscope (AFM) images were recorded by using a NanoScope (Veeco Instruments). An AFM sample was prepared by dipping a freshly cleaved mica substrate into a SWNTs/biosurfactant solution for a few seconds, followed by rinsing with water twice and then drying in vacuum.

Results and Discussion

Chemical-structure dependence: The solubilization ability of SWNTs in aqueous micelles (1 wt%, except MEGA-10=

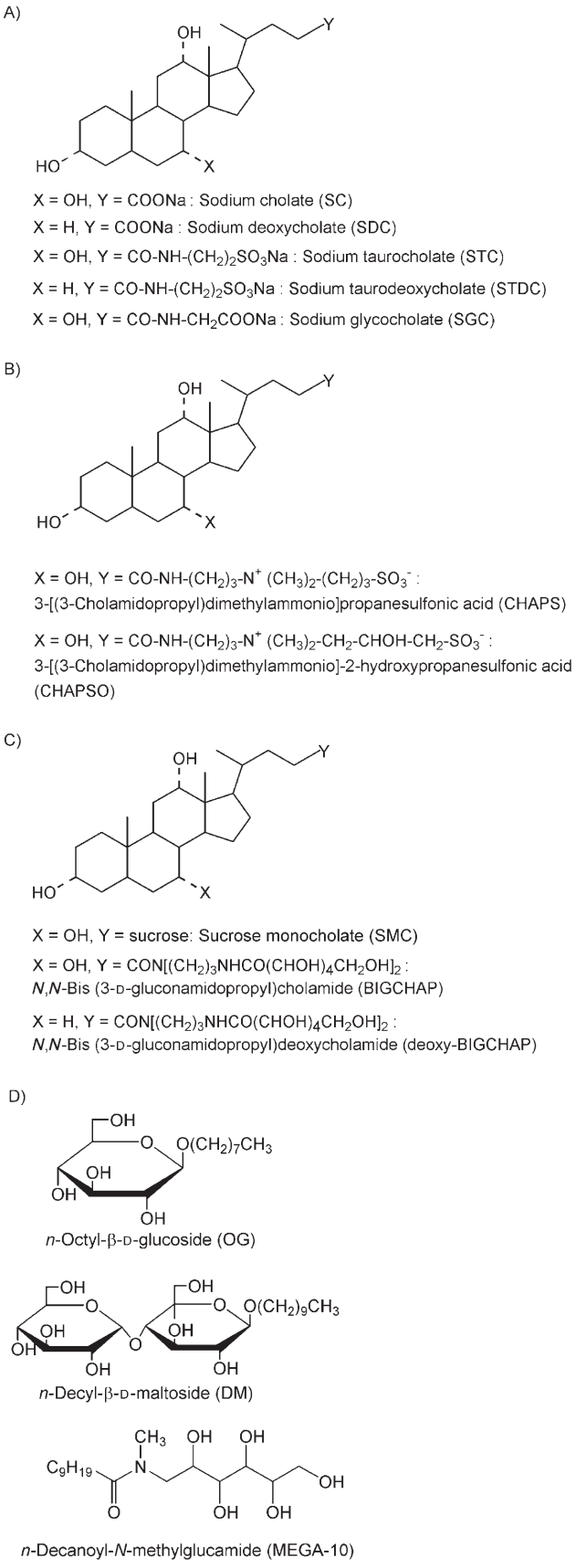

Figure 1. Chemical structures of steroid-type anionic surfactants (A), steroid-type zwitterionic surfactants (B), steroid-type nonionic surfactants (C), and sugar-type surfactants (D).

7.2 mM) of the thirteen biosurfactants was examined. Photographs and the visible/near-IR spectra for the solutions prepared as described above are shown in Figures 2 and 3, respectively. All the anionic-steroid biosurfactants, including SC, SDC, STC, STDC, and SGC, solubilized the SWNTs well and the solutions were stable for more than six months.

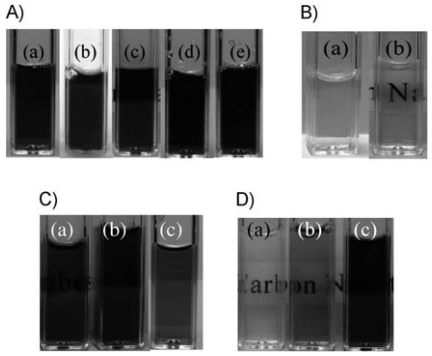

Figure 2. Photographs of SWNTs dissolved in aqueous solution containing a given biosurfactant (1 wt%, except MEGA-10 = 7.2 mM). Biosurfactants used: A) SC (a), SDC (b), STC (c), STDC (d), SGC (e); B) CHAPS (a), CHAPSO (b); C) BIGCHAP (a), deoxy-BIGCHAP (b), SMC (c); D) OG (a), DM (b), MEGA-10 (c).

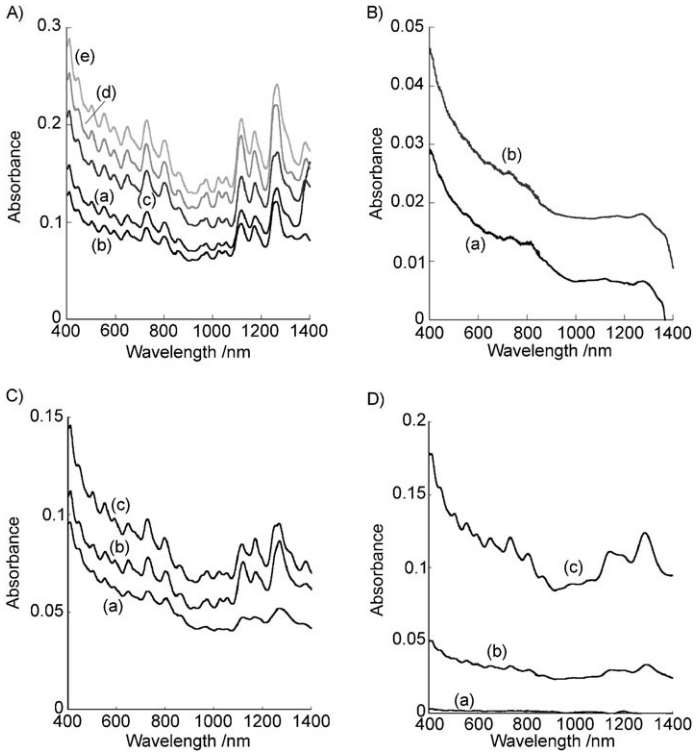

Figure 3. Visible/near-IR spectra of the SWNTs dissolved in 1 wt% aqueous solutions of given biosurfactants. Biosurfactants used: A) anionic steroid-type biosurfactants SC (a), SDC (b), SGC (c), STDC (d), STC (e); B) zwitterionic steroid-type biosurfactants containing CHAPS (a), CHAPSO (b); C) nonionic steroid-type biosurfactants containing SMC (a), deoxy-BIGCHAP (b), BIGCHAP (c); D) sugar-type biosurfactants containing OG (a), DM (b), MEGA-10 (c). Concentration of biosurfactants was 1 wt% in water, except MEGA-10 = 0.3 wt% (7.2 mM). Optical-cell length, 1 mm. Temperature, 25°C.

Characteristic absorption bands in the near-IR region, due to the interband transition between the mirror image spikes in the density of states (DOS) of the SWNTs,[17] are clearly visible and their shapes are virtually identical to those for the individually dissolved SWNTs in the micelles of SDS.[18] This indicates that the aqueous micelles used here have the ability to individually dissolve the SWNTs. Among them, STC and STDC possess the highest abilities to solubilize the SWNTs. In sharp contrast, as shown in Figures 2B and 3B, the solubilization ability of CHAPS and CHAPSO, both zwitterionic surfactants, toward the SWNTs was considerably lower than those of the five anionic steroid surfactants (A). Clearly, the charge of the side chain on the surfactants plays a crucial role in the solubilization of the SWNTs. The absorbances in the near-IR spectra of the SWNTs dissolved in the deoxy-type surfactants, SDC and STDC, were somewhat lower than those of the corresponding oxy-type surfactants (Figure 3).

We next compared the SWNT-solubilization ability of six different nonionic biosurfactants, including three steroid-type surfactants SMC, BIGCHAP, and deoxy-BIGCHAP, and three sugar types DG, DM, and MEGA-10. As can be seen in Figure 2C and D; 1) BIGCHAP shows the highest solubilization of these compounds, and the spectra in the first semiconducting region (1100–1400 nm) are sharp, suggesting the existence of individually dissolved SWNTs, ii) the solubilization abilities of DM and GM are not very high, and iii) OG had almost no ability to dissolve the SWNTs. It is evident that the sugar surfactants also showed a strong chemical-structure dependence for the solubilization/dispersion of the SWNTs. Unfortunately, it is difficult to explain the strong chemical-structure dependence at the molecular level, while the structures of micelles might be important for the dissolution of the SWNTs in water. The amounts of SWNTs dissolved in the micellar solutions estimated from the absorption of the near-IR spectra were: 82 (for SC), 70 (for SDC), 151 (for STC), 132 (for STDC), 113 (for SGC), 10 (for CHAPS), 21 (for CHAPSO), 2 (for OG), 28 (for DM), 77 (for BIGCHAP), 68 (for deoxy-BIGCHAP), 50 (for SM), and 58 $\mu g\,mL^{-1}$ (for MEGA-10).

Effect of cmc: The effect of the cmc on solubilization was examined by using the anionic steroid biosurfactants SC, STC, STDC and SGC, and nonionic biosurfactants SMC, BIGCHAP, deoxy-BIGCHAP, DM, OD, and MEGA-10. Photographs of the solubilized SWNTs in these solutions and their visible/near-IR absorption spectra are shown in Figures 4 and 5. The steroid biosurfactants SC, SMC, BIGCHAP, and deoxy-BIGCHAP dispersed/dissolved the SWNTs at concentrations below their cmc values,[19] while the absorbance of the solutions were lower than those of their 1 wt% micellar solutions, and the first semiconducting bands were somewhat broader than those of their micellar solutions. The SWNTs were also dissolved/dispersed in 1 mM aqueous solutions of BIGCHAP, deoxy-BIGCHAP, and MEGA-10. In contrast, the SWNT solubility in 1 mM SMC was much lower, and the SWNTs were not dissolved/dis-

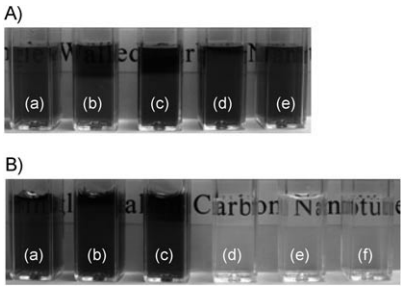

Figure 4. Photographs of SWNTs dissolved in aqueous solution containing a given biosurfactant (1 mM). Biosurfactants used: A) SC (a), SDC (b), STC (c), STDC (d), SGC (e); B) SMC (a), BIGCHAP (b), deoxy-BIGCHAP (c), OG (d), DM (e), MEGA-10 (f).

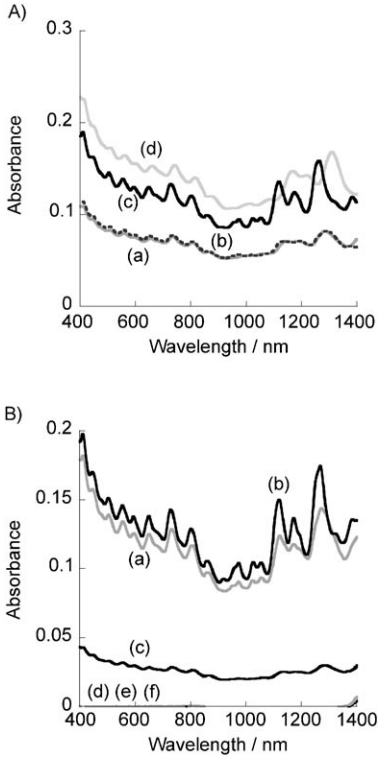

Figure 5. Visible/near-IR spectra of SWNTs dissolved in aqueous solution containing a given biosurfactant (1 mM). Biosurfactants used: A) anionic biosurfactants SC (a), SGC (b), STDC (c), STC (d); B) nonionic biosurfactants BIGCHAP (a), deoxy-BIGCHAP (b), SMC (c), OG (d), DM (e), MEGA-10 (f). Optical-cell length, 1 mm. Temperature, 25 °C.

persed in 1 mM solutions of DM and OG. The SWNT solubility in the 1 mM solutions is derived from the adsorption of these molecules onto the surfaces of the SWNTs. The sugar surfactants DM and OG that have long chains are expected to have very low affinity for adsorption onto the surface of the SWNTs. In contrast, the steroid biosurfactants used here can disperse/dissolve the SWNTs even at concentrations below their cmc. As described above, the steroid biosurfactants have a hydrophobic, rigid steroid backbone, which could facilitate adsorption onto the surfaces of the SWNTs, resulting in the solubilization of the SWNTs in water.

Figure 6 shows the visible/near-IR absorption spectra of SWNTs dissolved/dispersed in four different SC concentrations (1–50 mM). The amount of solubilized SWNTs in-

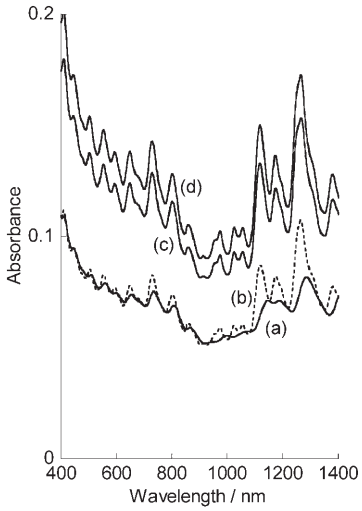

Figure 6. Visible/near-IR spectra of SWNTs dissolved in aqueous solutions of SC. Concentrations of SC: 1 mM (a), 14 mM (b), 20 mM (c), 50 mM (d). Optical-cell length, 1 mm. Temperature, 25 °C.

creased as the concentration increased, although the overall increase in dissolved SWNTs was very small; for example, the amount of the SWNTs dissolved in 50 mM SC was only twice that dissolved in 1 mM SC. The interesting feature is that the spectral shapes below and above the cmc are quite different, namely, the spectrum at concentrations below the cmc was very broad. Aqueous solutions of the SWNTs dissolved/dispersed in 1 mM, 14 mM, and 50 mM SC were placed on glass substrates and then air-dried to obtain three different solid SWNTs/surfactants, whose Raman spectra were measured (Figure 7). Clearly, the semiconducting peak in the 1 mM solution is weaker than those in the more concentrated solutions, although the intensities at 260 cm^{-1}, which are from the metallic SWNTs, are comparable. These results suggest the selective extraction of the metallic SWNTs by using 1 mM SC, although the selectivity between the semiconducting and metallic SWNTs is not high.

AFM study: A typical AFM image of SWNTs dissolved in a micelle of the biosurfactant STC is shown in Figure 8. From the height profiles of the AFM images, the diameters of 50 nanotubes were found to be in the range 0.7–1.3 nm (Figure 9). Because this diameter range is virtually the same as that of the used SWNTs, this indicates that almost all SWNTs were solubilized individually in the solution. In contrast, AFM images for SWNTs dispersed in 1 mM STC gave both individually dissolved SWNTs and bundled SWNTs whose heights were ≈20–30 nm (data not shown).

Chirality index of SWNTs: Smalley et al.,[18] Weisman et al.,[20] and Maruyama et al.[21] have reported that the as-

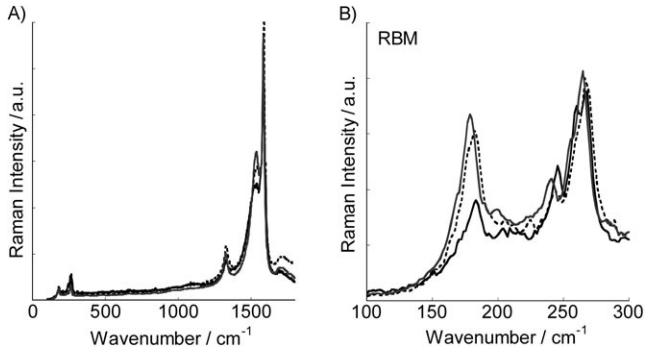

Figure 7. Raman spectra of SWNTs dissolved in aqueous solution containing SC: A) 100–1800 cm^{-1}, B) 100–300 cm^{-1}. Concentrations of SC: 1 mM (black line), 14 mM (dashed line), 50 mM (gray line).

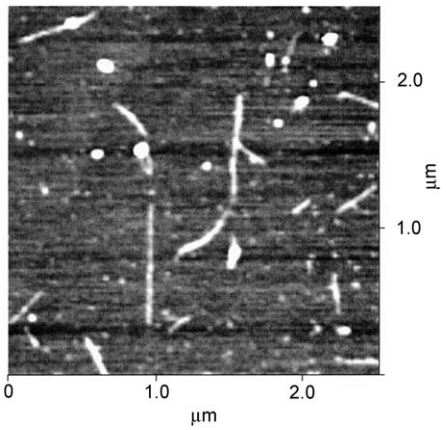

Figure 8. AFM image of SWNTs dissolved in a micelle of STC (1 wt%) on mica.

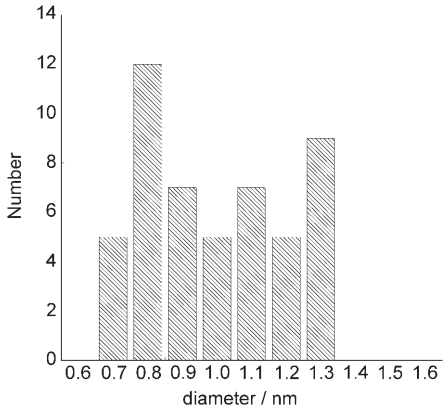

Figure 9. Height distribution of the AFM images for a SWNT/STC micellar solution.

produced SWNTs dissolved individually in an aqueous micelle of SDS show photoluminescence in the near-IR region. Consequently, considerable attention has been focused on these unique optical behaviors. In this study, we examined the near-IR photoluminescence behaviors of the SWNTs in 1 wt% and 1 mM SC, STC, SGC, and BIGCHAP solutions. The contour plots of the excitation wavelength (500–900 nm)/emission wavelength (900–1300 nm) profiles for these solutions are demonstrated in Figure 10. The contour plots for the SWNTs in 1 wt% SC showed the existence of SWNTs with chirality indices of (7,6), (8,4), (8,6), (9,4), and (9,5), the behavior of which is virtually identical to that of the SDS-dissolved SWNTs,[20,21] (Figure 10A, left). The results with STC and SGC (both 1 wt%) proved the significant presence of SWNTs with the chirality indices of (7,5), (7,6), (8,4), (8,6), and (9,4), and (7,5), (7,6), (8,4), and (9,4), respectively (Figure 10B and C, left). As seen in Figure 10D, left, the micelle of BIGCHAP produced a different pattern, indicating that this solution is rich in SWNTs with chirality indices (8,6) and (9,5). Because of the sugar side chain, the micellar structures of BIGCHAP would be different from those of SC, STC, and SGC. Despite the broadness in the near-IR absorption spectra obtained for their 1 mM solutions, the near-IR photoluminescence spectra could be detected, indicating that individually dissolved SWNTs exist in these solutions (Figure 10, right side). The contour plots for SWNTs in 1 wt% and 1 mM solutions of SC were almost identical (Figure 10A). In contrast, the contour plots between micellar (1 wt%) and non-micellar (1 mM) solutions of STC, SGC, and BIGCHAP were somewhat different (Figure 10B–D). This difference would be due to the difference of solubilization mechanisms. The contour plots of SWNTs in 1 mM SGC were complex, that is, the following three patterns for 1 mM SGC were detected: the (7,5), (7,6), and (8,4)-rich pattern (Figure 10C, right), the (7,6), (8,4), (8,6), (9,4), and (9,5)-rich pattern, and the (6,5) and (8,3)-rich pattern (data not shown). The solubility of SGC in water is low, and this might be related to the solubilization behaviors of the SWNTs.

Effect of pH: Finally, we examined the effect of pH on the SWNTs dissolved in aqueous solutions of the acidic biosurfactants SC, SDC, STC, STDC, and SGC. The addition of concentrated HCl to these solutions caused precipitates to form, which were collected on filter paper (Membrane Filter, pore size: 0.1 mm) and then air-dried. Resolubilization of the collected solid products in water (pH > 6) was carried out by sonication using a bath-type sonicator for 5 min. The visible/near-IR absorption spectra of the resolubilized solutions were virtually identical to those of the solutions before HCl addition (data not shown), indicating that no centrifugation is required to obtain the individually dissolved SWNTs in water. In addition, a very short sonication time (5 min or less) was sufficient for preparation of the resolubilized SWNT solutions. The solid state SWNTs/biosurfactant nanocomposites are useful nanomaterials for the preparation of individually dissolved SWNTs in water, and might be applicable in many areas of nanoscience.

Solubilization mechanism: The mechanism for the solubilization of SWNTs using biosurfactants at concentrations above the cmc would be similar to that of the so-called "micellar solubilization" using surfactants, such as SDS.[18] The

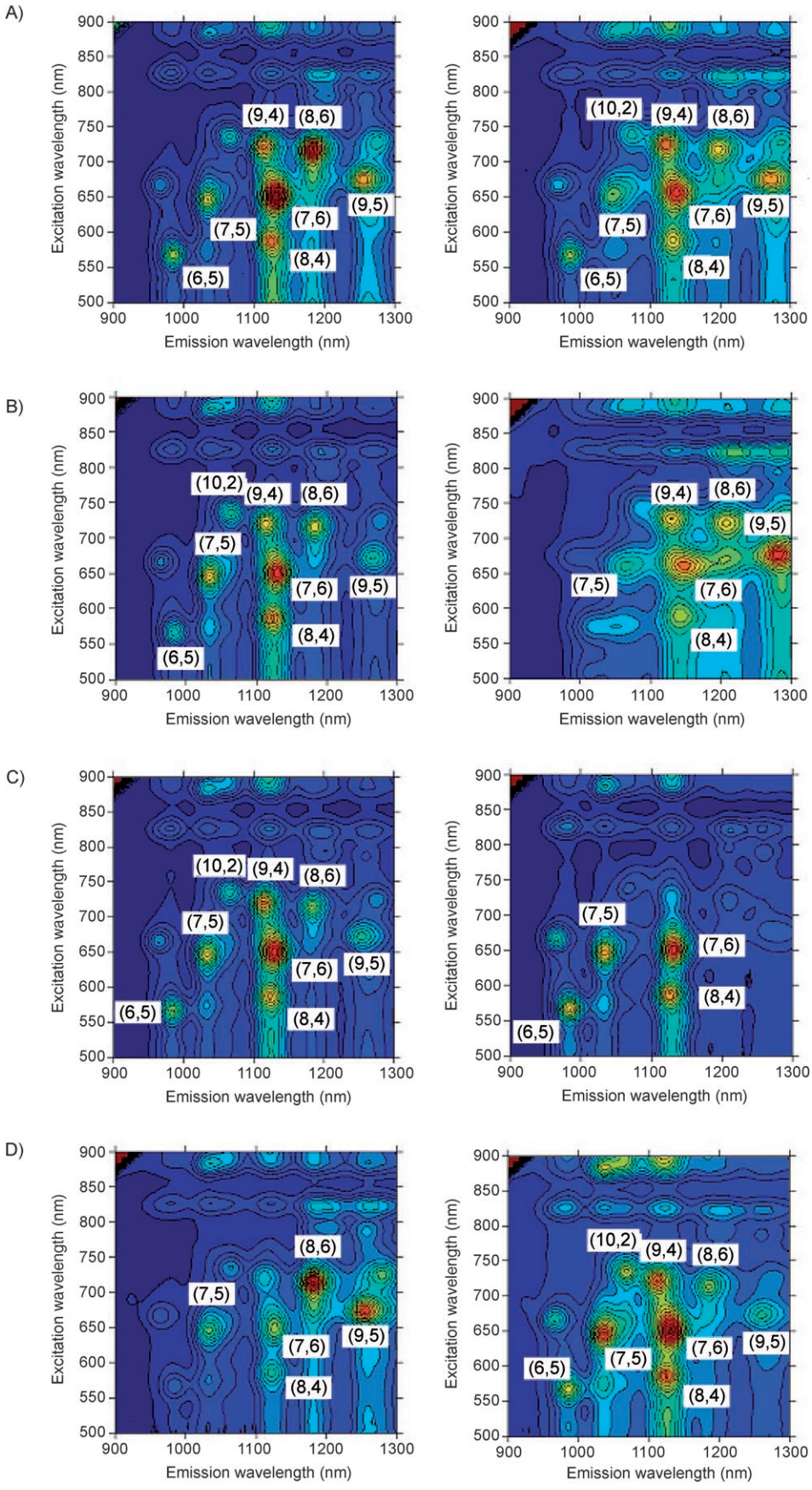

Figure 10. Contour plots of photoluminescence spectra as a function of excitation wavelength and the resultant emission. A) 1 wt% SC (left), 1 mM SC (right); B) 1 wt% STC (left), 1 mM STC (right); C) 1 wt% SGC (left), 1 mM SGC (right); D) 1 wt% BIGCHAP (left), 1 mM BIGCHAP (right).

solubilization should be due to physisorption of the biosurfactants onto the surfaces of the SWNTs, as the surfactants have no chemically reactive groups, unlike SDS, to react chemically with the SWNTs. We conducted a dialysis experiment for a SWNTs/SC (1 wt%) aqueous solution by using membrane tubing (molecular-weight cutoff 3500, Spectrapor Spectrum Medical Industries). SC gradually leaked from the inside of the tubing to the outer water phase and caused precipitation of the SWNTs in the tubing. However, as shown in Figure 11, even after two days of dialysis, about 15% of the SWNTs remained in the tubing as a transparent solution/dispersion. After dialysis, the near-IR absorption spectrum became somewhat broader, indicating that the SWNTs form a bundled structure in water that does not contain any free SC molecules. The observed phenomenon would be due to the adsorption of SC molecules onto the surface of the SWNTs. A possible model for the adsorption of a steroid surfactant is presented in Figure 12. The steroid biosurfactants have a large, rigid, and planar hydrophobic moiety of a steroid nucleus with two or three hydroxyl groups. This unique structure would be important for adsorption onto the surfaces of the SWNTs, leading to preparation of transparent disper-

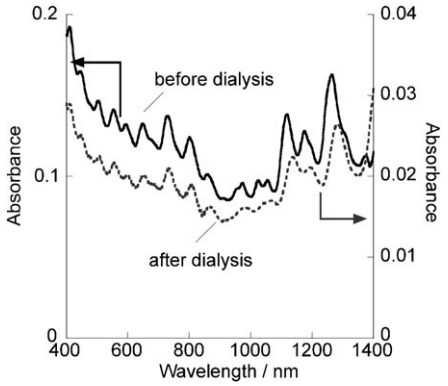

Figure 11. Visible/near-IR spectra of SWNTs dissolved in aqueous solutions of SC before and after dialysis. Optical-cell length, 1 mm. Temperature, 25 °C.

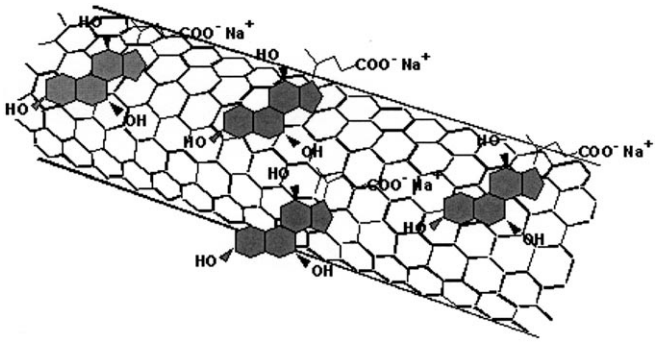

Figure 12. Model for the adsorption of a steroid surfactant onto the surface of SWNTs.

sions of SWNTs in water that does not contain any free steroid molecules.

Conclusion

We analyzed the solubilization behaviors of SWNTs in aqueous micellar solutions and in the 1 mM (below cmc) solutions of thirteen anionic, zwitterionic, and nonionic biosurfactants, such as cholate derivatives and sugar-type biosurfactants. Interesting observations were: 1) a strong chemical-structure dependence of the individual dissolution of the SWNTs, 2) the individual dissolution of the SWNTs was possible at concentrations below the cmc of the biosurfactants, and 3) a narrower distribution of the SWNT chirality indices is possible in water containing a biosurfactant. We also presented a mechanism for the dispersion of SWNTs below the cmc of the biosurfactants. Solid nanocomposites of SWNTs and acidic biosurfactants obtained under acidic conditions may be applicable in many fields of nano(bio)chemistry, as the nanocomposites readily produce individually dissolved SWNTs in water.

Acknowledgements

We thank Prof. Hiroyuki Furuta for the use of the Horiba Spex Fluorolog-NIR spectrofluorometer. This work was supported by Nano Carbon Technology Project supported by NEDO, the Grant-in-Aids from the Ministry of Education, Science, Sports, and Culture, Japan, and Kyushu University Interdisciplinary Programs in Education and Projects in Research Development.

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Received: March 8, 2006
Published online: July 6, 2006

