

Thermodynamics of the Exchange of Solubilizers on Single-walled Carbon Nanotubes

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The thermodynamics of the exchange of solubilizers adsorbed on single-walled carbon nanotubes (CNTs) is probed by analysis of the spectral shifts of the CNTs in the near-infrared region. Equilibrium constants and thermodynamic parameters of the exchange of sodium cholate for DNA (20-mers of oligo DNAs, cytosine) on CNTs of different chirality are determined.

Single-walled carbon nanotubes (CNTs) are rolled-up graphene sheets with rigid one-dimensional structures. The diameter and optical band gap of CNTs are uniquely related to their chiral indices (n,m), which represent how the graphene sheets are rolled up.¹ Evaluation of the interactions between molecules and CNTs has attracted much research.^{2–4} There have been several reports focused on this topic by monitoring fluorescence quenching induced by adsorption onto CNTs,^{5,6} the absorption of adsorbed dye on CNT-coated silica spheres,⁷ and Raman shifts induced by adsorption of CNTs⁸ and by chromatography-based analysis using CNTs as the stationary phase.^{9,10} However, quantitative evaluation of the interaction between molecules and CNTs has been very limited.

Exchange of CNT solubilizers has been used to prepare individually solubilized CNTs^{11–13} and separate CNTs with a different chirality.^{14–16} The benefit of this method is that it does not require sonication, so destruction or denaturation of the CNTs is avoided. Furthermore, the exchange of the solubilizers adsorbed on the CNTs is important to understanding the interaction between molecules and CNTs.

Here we describe the thermodynamics of the exchange of solubilizers adsorbed on the CNTs based on the analysis of the shifts in the near-IR (NIR) absorption spectra of the CNTs. The equilibrium constants (K_a) and thermodynamic parameters, such as enthalpy (ΔH) and entropy (ΔS) of the solubilizer exchange of sodium cholate (SC) with oligo-DNA (20-mers of cytosine) on the CNTs are determined. The dependence of tube diameter on K_a and changes in ΔH and ΔS are also described. In order to prove our presented thermodynamic treatment, we used SC and oligo-DNA, which are well-known CNT solubilizers.

As CNTs, HiPco-CNTs (Unidym) were used in this study. The CNTs were dissolved in aqueous micelles of SC (denoted SC-CNTs) (see the Supporting Information for experimental details).¹⁷ Experimental conditions to obtain individually solubilized CNTs were the same as those reported previously.^{18–20} The concentration of SC ([SC]) was adjusted to 2 mM, while the concentration of the DNA ([DNA]) ranged from 0–15.6 μM . All of the solutions contained phosphate buffer (pH 11.5, 20 mM). The solutions were stored for one day at a temperature of 15, 30, 35, or 40 °C, then absorption spectra were measured using a

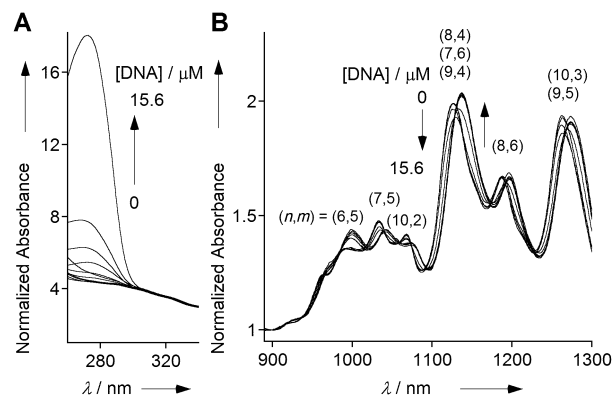


Figure 1. Absorption spectra of the CNTs dissolved in solutions containing SC in the absence and presence of the DNA (30 °C). A: the UV region, B: the NIR region. The pair of integers (n,m) written near the peak tops in B indicate the chirality of the CNTs.

V-670 spectrophotometer (JASCO) equipped with a temperature controller (ETCS-761).

Figure 1 shows the absorption spectra of the solutions of CNTs in the absence and presence of the DNA at 30 °C; in Figure 1A (the UV region), the absorption peaks from the DNA are observed. Figure 1B (the NIR region) shows absorption peaks consistent with the S11 transitions of the semiconducting CNTs,²¹ which allowed the chirality of the CNTs to be assigned.²¹ The absorption peaks of the CNTs exhibited a red shift as the [DNA] increased; that is, the intensity of the absorption peaks of the SC-CNTs decreased and new peaks appeared about 10-nm red-shifted from the original peaks. These spectral changes are accompanied by the isosbestic points as can be seen in the figure. This signifies that there are two species in the solution: the SC-CNTs and the DNA-solubilized CNTs (DNA-CNTs). These species exist in equilibrium in the mixed solutions containing both SC and the DNA. The equilibrium constant (K_a) of these CNTs with a different atmosphere can be calculated using the following equation:

$$K_a = \frac{[\text{DNA-CNT}][\text{SC}]}{[\text{SC-CNT}][\text{DNA}]} \quad (1)$$

The ratio of [SC-CNT] to [DNA-CNT] in the solutions containing both SC and the DNA were estimated from the absorption spectra (see the Supporting Information Results and discussion details).¹⁷ Briefly, the absorbance peaks for [DNA] = 15.6 μM and [DNA] = 0 μM were assumed to be peaks signifying [DNA-CNT] and [SC-CNT], respectively. The

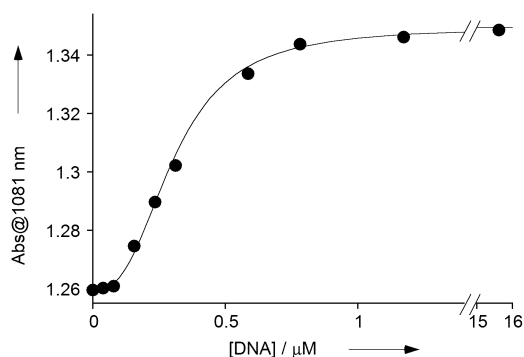


Figure 2. Absorbance of the DNA-CNT solutions (filled circles) and fitting curves (solid line) plotted against the [DNA] at 30 °C.

six peaks in Figure 1B were analyzed independently. For example, the absorbance at 1081 nm (Abs@1081 nm) was used to estimate the exchange of solubilizers on the (10,2)CNTs.

The obtained [SC-CNT] and [DNA-CNT] were fitted using the Hill equation to calculate the equilibrium constants (K_a) of the exchange following the method used by Papadimitrakopoulos et al. for the exchange of flavin mononucleotides and sodium dodecylbenzenesulfonate (SDBS).¹⁴ Based on their report, we obtained the following equation:

$$\Delta A = [\text{DNA-CNT}] = \frac{[\text{DNA}]^n}{\left(\frac{[\text{SC}]}{K_a}\right)^n + [\text{DNA}]^n} \quad (2)$$

where n corresponds to the Hill coefficient reflecting the cooperativity of the exchange reaction.

Figure 2 shows a plot of Abs@1081 nm against [DNA] at 30 °C. The fitting curve was obtained using eq 2. The K_a and n of the exchange reaction on the (10,2)CNTs were determined to be 6.6×10^3 and 2.7, respectively. In previous reports,^{14,16} exchange of flavin with SDBS also showed positive n values (3 to 16) at room temperature. In that case, formation of aqueous micelles of SDBS was the origin of such cooperativity. On the contrary, in our case, the concentration of the DNA was varied; thus, the cooperativity observed for the exchange of SC with the DNA does not originate from micelle formation. Previous papers have reported that SC is densely packed^{22,23} and that DNA wraps with a helical structure²⁴ on CNTs. Desorption of densely packed SC from the CNTs, which is induced by the polyanionic DNA, is probably cooperative. The smallest (6,5)CNTs, which possess a diameter of 0.76 nm, showed smaller K_a and n than those of the other chirality indices. The small diameter of the (6,5)CNTs probably affected cooperative desorption of the SC molecules self-assembled on the CNTs.

K_a and n at 15 and 40 °C are shown in Table 1 (for detailed Experimental and the data that were used to determine the value in Table 1, see the Supporting Information, Figures S1–S9 and Table S1).¹⁷ Larger K_a values were obtained at the higher temperature. This means that the higher temperature enhances the exchange of SC with the DNA on the CNTs. On the other hand, n was independent of temperature.

Plots of $\ln K_a$ for the CNTs of each chirality against the inverse of temperature ($1/T$) are shown in Figure 3. The thermodynamic parameters ΔH , ΔS , and $T\Delta S$ at 25 °C were

Table 1. Equilibrium constants and Hill coefficients of the exchange of SC and the DNA on the CNTs of specified chiral index of (n,m)

Chiral index (n,m) of CNTs	$K_a \times 10^{-3}$			Hill coefficient n
	15 °C	30 °C	40 °C	
(6,5)	1.3 ± 0.1	1.8 ± 0.2	3.4 ± 0.4	1.3 ± 0.1
(7,5)	6.2 ± 0.7	9.9 ± 0.7	10.7 ± 2.4	2.8 ± 0.5
(10,2)	4.7 ± 0.2	6.6 ± 0.7	9.8 ± 1.6	2.5 ± 0.5
(8,4), (7,6), (9,4)	6.3 ± 0.6	7.6 ± 2.2	10.1 ± 2.1	2.7 ± 0.4
(8,6)	6.8 ± 0.7	8.8 ± 1.3	8.5 ± 2.3	2.4 ± 0.2
(10,3), (9,5)	6.5 ± 0.6	10.2 ± 1.6	11.7 ± 1.3	2.2 ± 0.3

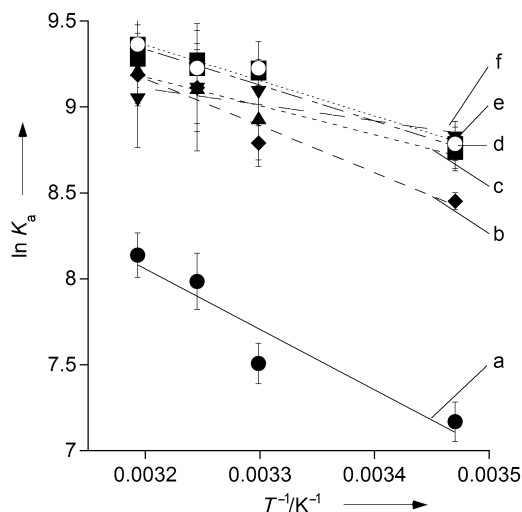


Figure 3. Temperature dependence of the thermodynamic equilibrium constants of solubilizer exchange on the CNTs having a specified chirality. a: (6,5), b: (10,2), c: (7,6), (8,4), (9,5), d: (7,5), e: (8,6), and f: (9,6), (10,3).

Table 2. Thermodynamic parameters ΔH , ΔS , and $T\Delta S$ at 25 °C obtained from linear analyses

Chiral index (n,m)	ΔH	ΔS	$T\Delta S/\text{kJ mol}^{-1}$
	/kJ mol ⁻¹	/kJ mol ⁻¹ K ⁻¹	25 °C
(6,5)	29 ± 7	0.16 ± 0.02	48 ± 7
(7,5)	17 ± 3	0.13 ± 0.01	40 ± 3
(10,2)	23 ± 4	0.15 ± 0.01	44 ± 4
(8,4), (7,6), (9,4)	14 ± 2	0.12 ± 0.01	36 ± 2
(8,6)	7.9 ± 3.2	0.10 ± 0.01	30 ± 3
(10,3), (9,5)	17 ± 2	0.13 ± 0.01	40 ± 2

obtained by fitting the plots and are presented in Table 2. The obtained ΔH and $T\Delta S$ at 25 °C ranged from 8 to 29 and 30 to 48 kJ mol⁻¹, respectively, indicating that the exchange reaction is entropy-driven. The positive ΔH means that the reaction is endothermic, which indicates that the π - π interactions between the nucleobases of the DNA and CNTs are weaker than the interactions between SC molecules and the CNTs. The large ΔS can be explained by desorption of SC molecules from the CNTs. Adsorption of the DNA on the CNTs increases ΔS .

For (6,5)CNTs, both ΔH and ΔS are larger than those of the CNTs with different chirality indices. Strano et al. suggested that

the number of SC molecules in a unit length of a CNT are independent of the chirality of the CNTs.²⁵ This means that the molecular assembly of SCs on the CNTs is not affected by the chirality (diameter) of the CNTs; therefore, the changes in enthalpy and entropy upon removing SC from the CNTs are almost independent of the chirality of the CNTs. Thus, the observed variation of ΔH , ΔS , and n probably arise from the degree of the interaction between the DNA and the CNTs. The obtained larger ΔH of the (6,5)CNTs can be assigned to the weak interaction between the DNA and the nanotubes. The larger ΔS and smaller n of the (6,5)CNTs are possibly explained by a weak interaction that would result from the large free volume of the DNA on the surface of the CNTs.

In conclusion, we have succeeded in the determination of K_a , n , ΔH , and ΔS for the exchange between SC and DNA on CNTs with different chirality. The thermodynamic parameters indicated that the exchange was entropy-driven and dependent on the chirality of the CNTs. The present study provides a fundamental feature in understanding thermodynamics of solubilized CNTs in solution.

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 21350110) (for NN), Grant-in-Aid for Scientific Research (B) (No. 21651053) (for YN), Grant-in-Aid for JSPS Fellows (No. 222032) (for YK) and the Global COE Program "Science for Future Molecular Systems" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

- R. Saito, M. Fujita, G. Dresselhaus, M. S. Dresselhaus, *Appl. Phys. Lett.* **1992**, *60*, 2204.
- H. Ozawa, T. Fujigaya, Y. Niidome, N. Hotta, M. Fujiki, N. Nakashima, *J. Am. Chem. Soc.* **2011**, *133*, 2651.
- H. Ozawa, T. Fujigaya, S. Song, H. Suh, N. Nakashima, *Chem. Lett.* **2011**, *40*, 470.
- H. Ozawa, N. Ide, T. Fujigaya, Y. Niidome, N. Nakashima, *Chem. Lett.* **2011**, *40*, 239.
- T. G. Hedderman, S. M. Keogh, G. Chambers, H. J. Byrne, *J. Phys. Chem. B* **2006**, *110*, 3895.
- S. Debnath, Q. Cheng, T. G. Hedderman, H. J. Byrne, *J. Phys. Chem. C* **2010**, *114*, 8167.
- J. Yoo, T. Fujigaya, N. Nakashima, *Chem. Lett.* **2011**, *40*, 538.
- S. Gotovac, H. Honda, Y. Hattori, K. Takahashi, H. Kanoh, K. Kaneko, *Nano Lett.* **2007**, *7*, 583.
- E. Menna, F. D. Negra, M. Prato, N. Tagmatarchis, A. Ciogli, F. Gasparri, D. Misiti, C. Villani, *Carbon* **2006**, *44*, 1609.
- J. Yoo, H. Ozawa, T. Fujigaya, N. Nakashima, *Nanoscale*, in press. doi:10.1039/c1nr10079c
- E. S. Jeng, P. W. Barone, J. D. Nelson, M. S. Strano, *Small* **2007**, *3*, 1602.
- E. S. Jeng, A. E. Moll, A. C. Roy, J. B. Gastala, M. S. Strano, *Nano Lett.* **2006**, *6*, 371.
- M.-H. Ham, J. H. Choi, A. A. Boghossian, E. S. Jeng, R. A. Graff, D. A. Heller, A. C. Chang, A. Mattis, T. H. Bayburt, Y. V. Grinkova, A. S. Zeiger, K. J. Van Vliet, E. K. Hobbie, S. G. Sligar, C. A. Wraight, M. S. Strano, *Nat. Chem.* **2010**, *2*, 929.
- S.-Y. Ju, J. Doll, I. Sharma, F. Papadimitrakopoulos, *Nat. Nanotechnol.* **2008**, *3*, 356.
- C. Backes, C. D. Schmidt, F. Hauke, A. Hirsch, *Chem.—Asian J.* **2011**, *6*, 438.
- C. Backes, U. Mundloch, C. D. Schmidt, J. N. Coleman, W. Wohlleben, F. Hauke, A. Hirsch, *Chem.—Eur. J.* **2010**, *16*, 13185.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- N. Nakashima, T. Fujigaya, *Chem. Lett.* **2007**, *36*, 692.
- A. Ishibashi, N. Nakashima, *Chem.—Eur. J.* **2006**, *12*, 7595.
- N. Nakashima, *Int. J. Nanosci.* **2005**, *4*, 119.
- S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, R. B. Weisman, *Science* **2002**, *298*, 2361.
- M. L. Usrey, E. S. Lippmann, M. S. Strano, *J. Am. Chem. Soc.* **2005**, *127*, 16129.
- M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, M. C. Hersam, *Nat. Nanotechnol.* **2006**, *1*, 60.
- M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. Mclean, S. R. Lustig, R. E. Richardson, N. G. Tassi, *Nat. Mater.* **2003**, *2*, 338.
- N. Nair, W.-J. Kim, R. D. Braatz, M. S. Strano, *Langmuir* **2008**, *24*, 1790.