Fluorescent Molecular Sensing for Various Types of Surfactants Using Amino-β-cyclodextrins Bearing Naphthalene Chromophore

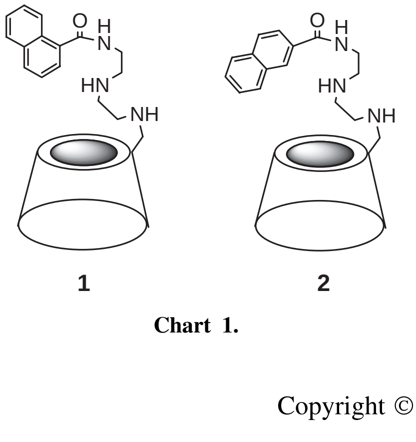
Hironori Nakashima and Noboru Yoshida*
Group of Molecular Materials Chemistry, Section of Environmental Materials Science,
Faculty of Environmental Earth Science, Hokkaido University, Sapporo 060-0810

(Received July 26, 2006; CL-060847; E-mail: nyoshida@ees.hokudai.ac.jp)

Fluorescent spectroscopic studies on the complexation of naphthalene-appended amino-β-cyclodextrins, **1** and **2**, with anionic, cationic, and nonionic surfactants have been carried out. In host **1**–surfactant system, an excellent fluorescent signal change was observed. On the other hand, host **2** exhibits no photophysical response in the presence of various surfactants. The difference in the properties between **1** and **2** was interpreted by difference in the inclusion depth of the naphthalene units for the cyclodextrin cavity. The binding abilities and thermodynamic (ΔH°, ΔS°, and ΔG°) quantities of **1**–surfactant system have been discussed to characterize structure/enegetics for the complexation process.

In recent years, a large variety of artificial molecules that act as fluorescent sensor received much attention in a broad area of chemistry, biology, technology, and medical science.[1,2] Particularly, the development of chemosensors based on cyclodextrins (CDx) is very interesting topic because of their high solubility and high affinities for various organic substrates in water.[3] For instance, fluorescent amino-β-cyclodextrin derivative **1** (Chart 1) which possesses very high solubility in water compared with native β-CDx, exhibits the possibility for a fluorescent anion sensor toward hydrophobic anions such as ClO_4^-.[4] From a point of view of environmental science, we have considered an application of this CDx derivative **1** to fluorescent sensing for the pollutants in an earth environment. We report herein the fluorescent sensing by host **1** for anionic (sodium 1-nonanesulfonate **G1**, sodium 1-decanesulfonate **G2**, sodium 1-dodecylsulfate, SDS **G3**), cationic (1-dodecyltrimethylammonium chloride, DTAC **G4**), and nonionic surfactants (triton X-100 **G5**, triton X-114 **G6**). The thermodynamic quantities in the host **1**–surfactant guests system are also reported.

The fluorescent spectral change of **1** upon addition of 1-decanesulfonate anion (**G2**) in aqueous solution is shown in Figure 1. Upon addition of **G2**, a gradual increase of fluorescence intensity (I_f) and a slight red shift in λ_{max} were observed. In contrast to this remarkable increase of I_f, no fluorescent response has been found in **2**–anionic surfactant system. Since the naphthalene unit of **2** is deeply included within the CDx cavity compared with that of **1**,[4] the guest inclusion into the cavity may be inhibited. The unexpected enhancement of I_f in **1**–surfactant guest system would be rationalized by the relatively increased rigidly and/or the subtle change in microenvironmental hydrophobicity around the naphthalene unit arising from cooperative host–guest complexation. The analyses of binding curves (ΔI_f vs. [guest]) using least-square method show 1:1 host–guest interaction.[3a] The binding constants (K_f) for the complexation with **G1**–**G6** are summarized in Table 1. It is noteworthy that the increase in extending chain length of anionic surfactants such as 1-nonanesulfonate anion (**G1**), 1-decanesulfonate anion (**G2**), and 1-dodecylsulfate anion (**G3**) leads to higher stability. These results indicate that hydrophobicity of the guest affects primarily on the stability of **1**–anionic surfactant complex. However, the binding constant of **1** with **G4** is much lower than that with **G3** which possesses the same alkyl chain length. This indicate the existence of electrostatic repulsion ($1\text{-NH}^+\cdots{}^+\text{N-}$**G4**) in **1**–**G4** binding. In contrast, the K_f values of **1**–**G5** and **1**–**G6** complexes are considerably high ($K_f = 13665$ and $14429\,\text{mol}^{-1}\,\text{dm}^3$, respectively). Harada et al., have suggested that the phenyl group of Triton X could form a complex with native β-CDx in aqueous solution.[5] In the cases of **1**–**G5** and **1**–**G6** system, the higher stabilities indicate that complexation may be occurred with including the phenyl group of Triton X into the CDx cavity of **1**.



1 **2**

Chart 1.

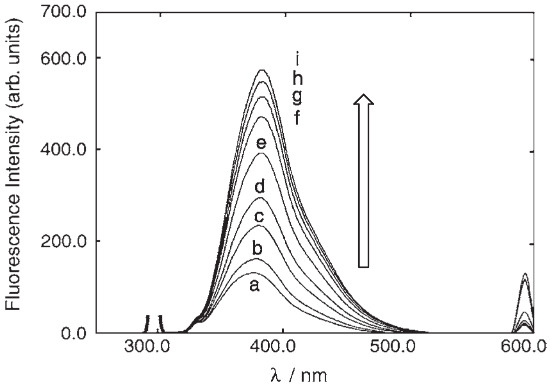


Figure 1. Fluorescence spectra of **1** in aqueous solution containing various concentration of 1-decanesulfonate anion (**G2**). [**1**] $= 1.25 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$, pH 7.0 and 298 K. $\lambda_{ex} = 295$ nm. [**G2**] = (a) 0, (b) 1.0×10^{-4}, (c) 5.0×10^{-4}, (d) 1.0×10^{-3}, (e) 2.5×10^{-3}, (f) 5.0×10^{-3}, (g) 1.0×10^{-2}, (h) 2.0×10^{-2}, (i) $3.0 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$.

In order to obtain more detailed information on complexation in the **1**–surfactant system, the thermodynamic parameters such ΔH°_{incl} and ΔS°_{incl} were determined from the van't Hoff

Table 1. Binding constants and thermodynamic parameters for inclusion reactions of **1** with various surfactants[a]

Guest	K_f/mol dm^{-3}	ΔG^o/kcal mol^{-1}	ΔH^o/kcal mol^{-1}	ΔS^o/cal mol^{-1} K^{-1}
$CH_3(CH_2)_8SO_3^-$ (**G1**)	268.7[b,d]	-3.30 ± 0.24	2.09 ± 0.12	18.1 ± 0.41
$CH_3(CH_2)_9SO_3^-$ (**G2**)	572.8[b,d]	-3.76 ± 0.04	-0.15 ± 0.02	12.1 ± 0.06
$CH_3(CH_2)_{11}OSO_3^-$ (**G3**)	2757.4[b,d]	-4.68 ± 0.14	0.09 ± 0.07	16.0 ± 0.23
$CH_3(CH_2)_{11}N^+(CH_3)_3$ (**G4**)	640.6[b,d]	-3.83 ± 1.06	1.21 ± 0.53	16.9 ± 1.79
Triton X-100 (**G5**)	13665[b,e]	-5.64 ± 1.40	-6.54 ± 0.69	-3.03 ± 2.39
Triton X-114 (**G6**)	14429[c,e]	-5.58 ± 0.30	-5.36 ± 0.15	0.74 ± 0.52

[a]Determined below the concentration of CMC. [b]At 298 K. [c]At 293 K. [d]$\lambda_{ex} = 295$ nm. [e]$\lambda_{ex} = 305$ nm.

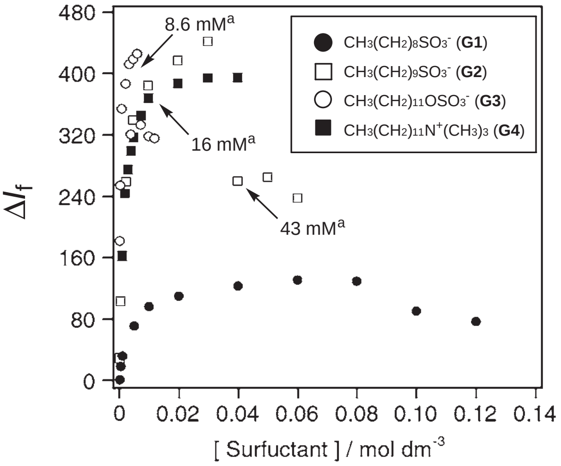


Figure 2. Flouorophotometric titration of **1** with various surfactants. [**1**] $= 1.25 \times 10^{-5}$ mol dm^{-3}, pH 7.0 and 298 K. [a]Critical micelle concentration (CMC) of anionic and cationic surfactants, see ref 6.

plots (log K_f vs. $1/T$).[4] The values of ΔH^o_{incl}, ΔS^o_{incl} and Gibbs energy term (ΔG^o_{incl}) are also listed in Table 1. It is noteworthy that enthalpic changes for inclusion of **1** with anionic surfactants are ca. zero or positive. The favorable entropic contribution (ΔS^o_{incl}) to the ΔG^o_{incl} term is larger than the enthalpic contribution, suggesting that complexation process between **1** and anionic surfactant is mainly controlled by hydrophobic interactions. To our knowledge, the $\Delta H^o_{incl} \approx 0$ and the mostly entropy-driven inclusion process by the CDx has not been found yet. Large positive ΔS^o_{incl} found in the **1**/**G1**–**G4** systems may be in part attributed to the partial aggregation of the guests at the smaller concentrations of the critical micelle concentration (CMC). In contrast, inclusion reactions of **1** with Triton X derivatives are enthalpically more favorable and entropically less favorable. Such a tendency in ΔH^o_{incl} may be attributed to the increase of van der Waals interactions for the complexation of **1** with the phenyl moiety of Triton X.

Figure 2 shows the fluorometric titration of **1** at various concentrations of **G1**, **G2**, **G3**, and **G4** in aqueous solution. It is interesting that the fluorescent intensity of **1** decreased drastically over the CMC of anionic surfactants. This fluorescent behavior of **1** was not observed by addition of excess of cationic and nonionic surfactants. The fluorescent change mechanism for the CMC detection is now unclear but considered to relate the electrostatic interaction between **1** and anionic surfactants (**1**-$NH^+\cdots{}^-SO_3$-**Guest**).

In conclusion, fluorescent amino-β-CDx **1** has shown the excellent fluorescent response on complexation with various surfactants. Furthermore, host **1** may be a powerful tool for the detection of CMC in aqueous solution. The application of **1** to fluorescent sensing for other organic pollutants is now in progress.

References

1 Reviews: a) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsonn, A. J. M. Huxley, C. P. McCoy, J. T. Rademachar, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515. b) R. Martinez-manez, F. Sancenon, *Chem. Rev.* **2003**, *103*, 4419. c) J. J. Lavigne, E. V. Anslyn, *Angew. Chem., Int. Ed.* **2001**, *40*, 3118. d) L. Prodi, F. Bolletta, M. Montalti, N. Zaccheroni, *Coord. Chem. Rev.* **2000**, *205*, 59. e) S. Uchiyama, A. P. de Silva, K. Iwai, *J. Chem. Educ.* **2006**, *83*, 720. f) R. Y. Tsien, *Am. J. Physiol.* **1992**, *263*, C723.

2 a) L. Fabbrizzi, M. Licchelli, F. Mancin, M. Pizzeghello, G. Rabaioli, A. Taglietti, P. Tecilla, U. Tonellato, *Chem. Eur. J.* **2002**, *8*, 94. b) M. D. Best, E. V. Anslyn, *Chem. Eur. J.* **2003**, *9*, 51. c) A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2002**, *8*, 4935. d) B. Garcia-Acosta, X. Albiach-Marti, E. Garcia, L. Gil, R. Martinez-Manez, K. Rurack, F. Sancenon, J. Soto, *Chem. Commun.* **2004**, 774. e) K. Hayashi, H. Akutsu, H. Ozaki, H. Sawai, *Chem. Commun.* **2004**, 1386. f) G. Bobba, J. C. Frias, D. Parker, *Chem. Commun.* **2002**, 890.

3 a) Y. Takenaka, M. Higashi, N. Yoshida, *J. Chem. Soc., Perkin Trans. 2* **2002**, 615. b) A. Ueno, *Supramol. Sci.* **1996**, *3*, 31. c) J. M. Haider, Z. Pikramerou, *Chem. Soc. Rev.* **2005**, *34*, 120. d) T. Ikeda, K. Yoshida, H.-J. Schneider, *J. Am. Chem. Soc.* **1995**, *117*, 1453. e) P. Choppinet, L. Jullien, B. Valeur, *J. Chem. Soc., Perkin Trans. 2* **1999**, 249. f) T. Tanabe, K. Touma, K. Hamasaki, A. Ueno, *Anal. Chem.* **2001**, *73*, 1877. g) S. Tamagaki, K. Batoh, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1389. h) A. Mulder, A. Jukovic, L. N. Lucas, J. van Esch, B. L. Feringa, J. Huskens, D. N. Reinhoudt, *Chem. Commun.* **2002**, 2734. i) M. Toda, N. Ogawa, H. Itoh, F. Hamada, *Anal. Chim. Acta* **2005**, *548*, 1. j) H. Ikeda, T. Murayama, A. Ueno, *Org. Biomol. Chem.* **2005**, *3*, 4262. k) T. Kuwabara, K. Shiba, M. Ozawa, N. Miyajima, Y. Suzuki, *Tetrahedron Lett.* **2006**, *47*, 4433.

4 H. Nakashima, Y. Takenaka, M. Higashi, N. Yoshida, *J. Chem. Soc., Perkin Trans. 2* **2001**, 2096.

5 A. Harada, H. Okumura, M. Okada, S. Suzuki, M. Kamachi, *Chem. Lett.* **2000**, 548.

6 M. J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd ed., Wiley-Interscience, New York, **1989**.

Published on the web (Advance View) September 16, 2006; doi:10.1246/cl.2006.1168