Roles of Axial Ligands on Intercalation of Cationic Metalloporphyrin into Smectite Clay Layers

Tsutomu Shiragami,* Keiko Nabeshima, Masahide Yasuda, and Haruo Inoue†
Department of Applied Chemistry, Faculty of Engineering, Miyazaki University, Gakuen-Kibanadai, Miyazaki 889-2192
†*CREST, JST (Japan Science and Technology)*

(Received October 28, 2002; CL-020908)

Adsorption and intercalation of +1 charged cationic dihydroxo(tetraphenylporphyrinato)antimony(V) bromide (**1a**) into an artificially synthesized smectite clay was studied. The red shift of Soret band of **1a** was observed in an aqueous clay suspension owing to the adsorption onto the clay. Analyses of X-ray diffraction of the obtained complex between **1a** and the clay indicate the intercalation of **1a** into the clay interlayer. Hydroxo group as an axial ligand led to the effective intercalation of **1a** into the clay.

Multilayered inorganic materials such as clays have been extensively studied from the viewpoints of two dimonsional reaction site for chemical reaction.[1] The adsorption and intercalation behaviors in interlayer surface have been investigated by photochemical method using a variety of dyes as guest molecules.[2] Especially, porphyrin and metalloporphyrin dyes are of interest because of their photochemical activity as well as their biochemical and catalytic functionality. Therefore, several studies on the interaction between porphyrin and cation exchangeable clays have recently reported.[3,4] In most reports, the porphyrins having +4 charged substitutes at meso-position (i.e. alkyl pyridinium salt) were used as a guest molecule. However, little is known about electrostatic 1:1 interaction between the cationic porphyrin guest and the anionic clays. The porphyrinatoantimony(V) molecules are a "+1 charged cationic complex" where the positive charge can delocalize in π-electron system of porphyrin ring[5] and have two axial ligands. They are a different type from the +4 cationic pyridinium-type porphyrin complexes. Here, we report on the adsorption and intercalation behaviors of porphyrinatoantimony(V) complexes (**1a–c**) into an artificially synthesized cation-exchangeable smectite clay (Sumecton SA; SSA), as shown in Figure 1.

The measurement of absorption spectra was performed for a solution prepared by mixing the aqueous solution of **1** ($5.0 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$)[5,6] with SSA ($(\mathrm{Na_{0.49}Mg_{0.14}})^{+0.77}[(\mathrm{Si_{7.20}Al_{0.80}})(\mathrm{Mg_{5.97}Al_{0.03}})\mathrm{O_{20}(OH)_4}]^{-0.77}$, Kunimine) solution ($50\,\mathrm{mg\,dm^{-3}}$).[4a,b] The loading level of **1** vs cationic exchange capacity of SSA (%LL) was adjusted by the addition of variable amounts of SSA to constant concentration of **1**. X-ray diffraction (XRD) analysis was performed for the samples prepared by filtration of the above mixture through a membrane filter (pore size = 1 μm) and drying at room temperature.

Figure 2 shows the absorption spectra of **1a–b** under the conditions of different %LL in aqueous SSA solution. At low %LL (10–20%), the $\lambda_{\max}$ of Soret band of **1a–b** was shifted from the $\lambda_{\max}$ (417 nm) without SSA to a longer wavelength (430 nm). As an increase of %LL, the further red shift of $\lambda_{\max}$ and the broading of Soret band were induced. Especially, the remarkable splitting of Soret band was observed in aqueous solution of **1a**-SSA complex at a high %LL (>40%), showing the strong interaction between the porphyrins each other. In the case of **1c**, similar spectral changes were observed. No absorption peaks of **1a–c** were detected in thier filtrates by the filtration **1**-SSA powders, and free **1a–c** whose $\lambda_{\max}$ of Soret band are 417 nm were observed in the aqueous SSA solution at a 120 %LL. These spectral changes clearly demonstrated the adsorption and aggregation of **1a–c** onto the surface or in the interlayer space of SSA, as have reported in the another dyes systems.[2]

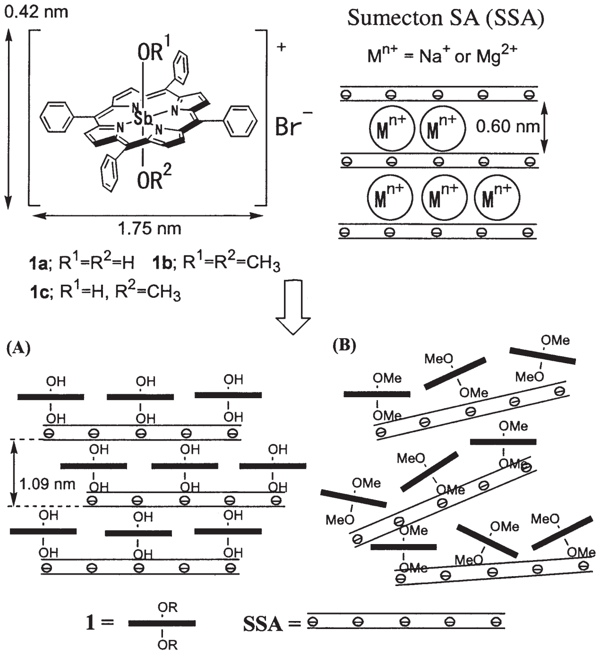

Figure 1. Schematic layered structure (A) and amorphous structure (B).

The interlayer distances for **1**-SSA powders obtained by filtration were estimated by XRD measurement. In the case of **1a**-SSA complex, some sharp diffraction peaks were observed by XRD measurement, indicating that the layer structure of SSA should be kept irrespective of the addition of **1a** (Figure 3(A)). As an increase of %LL, the interlayer distance of **1a**-SSA complex increase to reach 1.09 nm in more than 80 %LL, as shown in Figure 3(B). Judging from the interlayer distance being 0.60 nm for unmodified SSA, the increase of a net distance by the expansion was estimated to be 0.49 nm. According to X-ray crystallographic analysis of **1a**,[7] the thickness of **1a** for axial ligand direction was determined to be 0.42 nm. This value is almost consistent with the expanded interlayer distance of **1a**-SSA complex. These results strongly suggest that **1a** should be intercalated into SSA interlayer space at a high %LL, and that the orientation of the porphyrin plane should be almost parallel to the SSA clay layer, as shown in Figure 1(A). The orientation of **1a** was also evidenced by the fact that the spectral shape of Soret

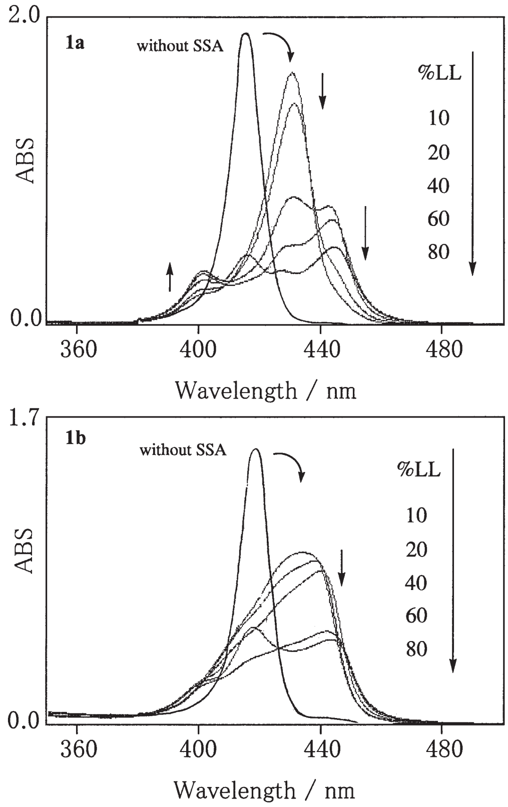

Figure 2. Absorption spectra of **1a** and **1b** at various %LL aqueous SSA solution.

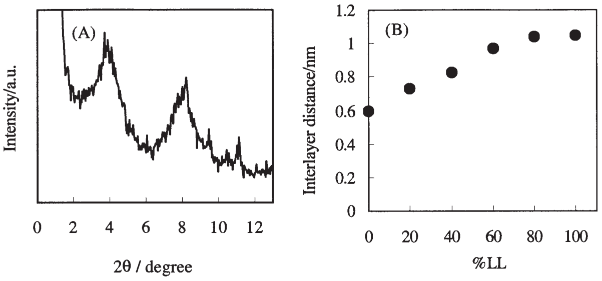

Figure 3. (A) The XRD profile of **1a**-SSA at %LL = 80%. (B) Relationship between the %LL and the interlayer distance determined by XRD measurement of **1a**-SSA.

band splitting showed the presence of porphyrin aggregates of edge-to-edge type.[8] If the orientation of **1a** is vertical to the clay layer, the expanded interlayer distance should be about 1.75 nm. On the other hand, XRD measurements for both **1b**- and **1c**-SSA complex gave no diffraction peaks, indicating that SSA should be amorphous by the addition of **1b** or **1c**, as shown in Figure 1(B). Accordingly, these results show that **1b**- and **1c**-SSA complex can not take the layer structure although the UV spectral change showed the adsorption of **1b–c** on SSA surface.

Thus, it is clear that the behaviors of adsorption and intercalation into the clay layer can be affected by the structure of axial ligand of cationic tetraphenylporphyrinatoantimony(V) complex. Two hydroxo groups as an axial ligand were effective for the intercalation into SSA. The forces for the formation of the intercalated structure can be attributed to hydrogen-bonding interaction between OH group at **1a** and the clay sheets as well as Coulombic attractive force. This is a first example for the intercalation of +1 charged cationic porphyrin complexes into the clay layer. The above results show the importance of the axial ligand structure as to how to control the intercalation of porphyrins.

This research was supported by a Grand-in-Aid for Scientific Research (No. 14050079) from the Ministry of Education, Science, Sports, and Culture.

References and Notes

1 a) J. K. Thomas, *Acc. Chem. Res.*, **21**, 275 (1998). b) J. K. Thomas, *Chem. Rev.*, **95**, 399 (1995). c) T, Kijima, *Thermochim. Acta*, **59**, 95 (1982).

2 a) K. Takagi and T. Shichi, in "Solid State and Surface Photochemistry," ed. by V. Ramamurthy and K. S. Schanze, Marcel Dekker, New York (2000), Vol. 5, p 31. b) K. Takagi and T. Shichi, *J. Photochem. Photobiol., C*, **1**, 113 (2000). c) H. Usami, K. Takagi, and Y. Sawaki, *J. Chem. Soc., Faraday Trans. 2*, **88**, 77 (1992). d) K. Takagi, T. Shichi, H. Usami, and Y. Sawaki, *J. Am. Chem. Soc.*, **115**, 4339 (1993).

3 a) S. S. Cady and T. J. Pinnavaia, *Inorg Chem.*, **17**, 1501 (1978). b) K. A. Carrado and R. E. Winans, *Chem. Mater.*, **2**, 328 (1990). c) H. Kaneyama, H. Suzuki, and A. Amano, *Chem. Lett.*, **1988**, 1117. d) E. P. Giannelis, *Chem. Mater.*, **2**, 627 (1990). e) I. Ukrainczyk, M. Chibwe, T. J. Pinnavaia, and S. A. Boyd, *J. Phys. Chem.*, **98**, 2668 (1994). f) Z. Chernia and D. Gill, *Langmuir*, **6**, 1350 (1999).

4 a) S. Takagi, T. Shimada, T. Yui, and H. Inoue, *Chem. Lett.*, **2001**, 128. b) S. Takagi, T. Shimada, M. Eguchi, T. Yui, H. Yoshida, D. A. Tryk, and H. Inoue, *Langmuir*, **18**, 2265 (2002). c) Z. Tong, T. Shichi, K. Oshika, and K. Takagi, *Chem. Lett.*, **2002**, 876.

5 a) T. Shiragami, K. Kubomura, D. Ishibashi, and H. Inoue, *J. Am. Chem. Soc.*, **118**, 6311 (1996). b) T. Takagi, M. Suzuki, T. Shiragami, and H. Inoue, *J. Am. Chem. Soc.*, **119**, 8712 (1997). c) Y. Andou, K. Shima, T. Shiragami, and M. Yasuda, *Chem. Lett.*, **2001**, 1198. d) T. Shiragami, Y. Andou, Y. Hamsuna, F. Yamaguchi, K. Shima, and M. Yasuda, *Bull. Chem. Soc. Jpn.*, **75**, 1577 (2002). e) Y. Andou, K. Ishikawa, K. Shima, T. Shiragami, M. Yasuda, and H. Inoue, *Bull. Chem. Soc. Jpn.*, **75**, 1757 (2002).

6 **1c**: Yield 90%; UV-vis (MeCN) λ_{max}/nm (log ε): 417 (5.72), 550 (4.26), and 590 (4.05); SIMS: m/z 781 (M^+); ^1H NMR ($CDCl_3$/ppm) δ −2.27 (3H, s, OCH_3), 7.81–8.01 (12H, m, Ph), 8.30 (4H, d, $J = 6.7$ Hz, Ph), 8.56 (4H, d, $J = 6.7$ Hz, Ph), 9.41 (8H, s, pyrrole).

7 The X-ray crystallographic data of **1a**: $C_{44}H_{30}N_4O_2SbBr$, $M_r = 847$, monoclinic, $P2_1$(No. 4), $a = 9.6418$ Å, $b = 8.4483$ Å, $c = 21.2765$ Å, $\beta = 98.1°$, $V = 1714$ Å^3, $Z = 2$, $D_{calcd} = 1.64$ g/cm^3, $D_m = 1.46$ g/cm^3, $R = 0.0548$, $R_w = 0.0441$.

8 a) M. Kasha, H. R. Rawls, and M. A. El-Bayoumi, *Pure Appl. Chem.*, **11**, 371 (1965). b) R. H. Jin, S. Aoki, and K. Shima, *J. Chem., Faraday Trans.*, **93**, 3945 (1997). c) K. Kano, T. Nakajima, and S. Hashimoto, *J. Phys. Chem.*, **91**, 6614 (1987). d) H. L. Anderson, *Inorg. Chem.*, **33**, 972 (1994).