OBERVATION OF THE INTERCALATION PROCESS OF A TETRA-CATIONIC PorphyrIN ACHIEVING HIGH MOLECULAR DENSITY WITHOUT AGGREGATION INTO AN ANIONIC CLAY FILM BY AN IMMERSION METHOD

TETSUYA SHIMADA, SHINGO ONODERA, SATOSHI HAMATANI, TAKUYA FUJIMURA, HARUO INOUE, and SHINOSKE TAKAGI

4Department of Applied Chemistry, Faculty of Urban Environmental Sciences, Tokyo Metropolitan University, Minami-ohsawa 1-1 Hachioji, Tokyo 192-0397, Japan
5Japan Society for the Promotion of Science, 5-3-1 Koujimachi, Chiyoda-ku, Tokyo 102-0083, Japan
6Center for priority areas, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan

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ABSTRACT

Several remarkable organic–inorganic multilayer hybrids, which include extremely high-density photosensitizer dyes, without aggregation have been produced using a method based on “size-matching intercalation” with a simple immersion technique. This study focuses on the intercalation process. Temporal progress of the intercalation of the +4-charged cationic porphyrin molecules in the interlayers of the anionic synthetic clay particles, which were fabricated into a thin transparent film, was observed by a spectroscopic method at various temperatures. The distance between the adjacent cations in the cationic porphyrin molecule was designed to be close to the average distance between the clay anionic sites, which is called the size-matching condition. When the loading amount of the porphyrin corresponded to 30% versus the cation exchange capacity (CEC) of the clay in a film, almost all the porphyrin molecules were intercalated into the clay film during a 10 h immersion. No aggregated species were observed at any time during the immersion. After the immersion, the average occupied area of one porphyrin molecule was estimated to be 8.3 nm². The time course of the intercalation was well simulated by a simple exponential function with a single time rate constant for each temperature condition. The Arrhenius plot of the rate was linear, and the Arrhenius activation energy estimated from the rate constants was 26.8 kJ mol⁻¹.

Key words: Porphyrin, Synthetic clay, Intercalation process, Thin film

INTRODUCTION

Nano-layered compounds have been studied over the last several years to construct functional materials, including dyes (Okada et al., 2012; Thomas, 2005; Shichi and Takagi, 2000; Suib, 1993). In particular, clay minerals, which are multilayered inorganic compounds and provide two-dimensional wide spaces, have attracted attention as host materials in organic–inorganic hybrids. However, the control of the adsorption behavior of dyes in the compounds is difficult because dye molecules tend to form aggregates on the solid surface (Miyamoto et al., 2000; Neumann et al., 2002; Bujdák, 2006; Schoonheydt, 2002; Bujdák et al., 2002; Arbeloa et al., 2007). Recently, we successfully produced interesting clay/porphyrin hybrid complexes, wherein the +4-charged cationic porphyrin molecules were densely adsorbed on the exfoliated clay sheets without aggregation (Takagi et al., 2002; Ishida et al., 2011). We demonstrated an efficient energy transfer between porphyrin molecules in the clay/porphyrin hybrids (Ishida et al., 2012; Shimada et al., 2013). The high-density adsorption of porphyrins was achieved when the distance between the adjacent cationic sites in the porphyrin was close to the average distance between the anionic sites on the clay surfaces (referred to as the size-matching condition). We believe that this size-matching condition is crucial for creating high-density adsorption without aggregation.

In addition to the hybrid of a porphyrin and an exfoliated clay sheet, we made a hybrid of a porphyrin and clay mul-
tilayer particle dispersed in water by a freeze-thaw method under the size-matching condition (Takagi et al., 2002). The porphyrin was densely intercalated in the interlayer of the clay particle. Recently, we successfully produced a hybrid clay film with a high density of +4 cationic porphyrin molecules intercalating without aggregation (Fujimura et al., 2013). This hybrid film was fabricated using an immersion method under the size-matching methodology. The immersion method is milder and more convenient than the freeze-thaw method. We were interested in the process of intercalation in the immersion process that did not form aggregated species, for example, whether any transient aggregated species form during the immersion. According to these reports (Takagi et al., 2002; Fujimura et al., 2013), remarkable characteristics were found at the intercalation of a +4 cationic porphyrin to clay: 1) the absorption spectrum of the intercalated cationic porphyrin is clearly different from that of the porphyrin in solution and that of the adsorbed species, 2) the inverse process of the intercalation was negligible, 3) the porphyrin could be intercalated without aggregation to the maximum amount, where the porphyrin cations neutralize the clay anions. These probably originated from the strong host–guest interaction of the porphyrin and clay. Because of characteristic 1), we expected that the monitoring of the intercalation could be easily performed using a spectroscopic method. In this study, we investigated the intercalation process of a +4 cationic porphyrin into a synthetic cation-exchangeable clay to understand its features using a spectroscopic method.

MATERIALS AND METHODS

In this study, the host material for intercalation was Smecton SA (SSA), which is a synthetic cation-exchangeable clay classified as saponite, while the guest was tetrakis (1-methyl-4-pyridiniumyl) porphyrin (TMPyP, Fig. 1), which has +4 cations. The average distance between the anionic sites of SSA is estimated to be 1.2 nm assuming a hexagonal array, while the distance between adjacent cationic sites of TMPyP was calculated to be 1.1 nm by the PM3 method. SSA obtained from Kunitake Industries was used without further purification. The tosylate salt of TMPyP was purchased from Aldrich, and the counter ion was substituted for chloride using an ion-exchange column. Deionized water prepared using the ORGANO BB-5A system (PF filter ×2 +G-10 column) was used. Dioxane and ethanol were purchased from Kanto Chemical Co., Inc. (spectral grade) and Nakarai Tesque, Inc. (special grade), respectively, and they were used without further purification.

The SSA thin film was prepared as follows. The SSA solution (100 mg L−1, water:dioxane = 4:1 (v/v)) was filtered through a membrane filter (pore size = 0.1 μm) under reduced pressure. A transparent SSA thin film was obtained by pressing the residue on a glass plate. A TMPyP solution (9 × 10−5 M) in mixed solvent (ethanol:water = 2:1 (v/v)) was prepared in a hermetic optical cell (1.0 cm2). The solution was stirred, and the SSA film was immersed in the solution for intercalation. The SSA film was stable during the immersion. The total amount of TMPyP in the solution corresponded to 30% versus the CEC of the SSA film. When all the TMPyP molecules were intercalated, the average occupied area of one porphyrin molecule was estimated to be 8.3 nm2. The SSA film containing TMPyP is henceforth referred to as the TMPyP/SSA hybrid film.

Absorption spectra of TMPyP in the solution and the TMPyP/SSA hybrid film were measured using a Shimadzu UV-2550 spectrophotometer. Two monitor-light paths were set; path (1) did not cross the film and path (2) crossed the film (Fig. 2). Absorption spectra of the film were obtained from the spectra of path 1 and path 2. The amount of absorption from the solution in path 2 was eliminated using the spectra of path 1 after correcting for the optical length. The temperature of the cell was maintained constant. Temporal changes of the absorption spectra of the film and solution were observed at 292 K, 303 K, 313 K, and at room temperature (298 K).

RESULTS

Figure 3 shows the absorption spectra of the solution and hybrid film after 90 min of immersion, observed at 303 K.
The absorption spectrum of the film has a maximum at 454 nm. This is supposed to be a spectrum of TMPyP intercalated in the swollen SSA film. We confirmed that the wavelength at a maximum absorbance of the hybrid films shifted under dry condition to 475.5 nm, which is close to that of the TMPyP/SSA intercalated in the complex obtained by a freeze-thaw method (Takagi et al., 2002). The drying caused the interlayer space of the swelling SSA to narrow and induced a further flattening of the intercalated TMPyP structure.

Figures 4a and 4b show the temporal change in the absorption spectra of the solution and TMPyP/SSA hybrid film observed at 303 K. The spectrum of the solution was monitored in the Soret band range (350-500 nm). On the other hand, the spectrum of the TMPyP/SSA hybrid was monitored in the Q-band range (500-700 nm) because the saturation of absorption was negligible even for films with a high density of TMPyP molecules over this range. Figure 4a indicates a monotonous decrease in the absorption spectrum of the solution. This change corresponds to a decrease of TMPyP in the solution because of intercalation. Almost all the TMPyP in the solution disappeared after 10 h. On the other hand, the absorption spectra of the TMPyP/SSA hybrid film show a monotonous increase with time. The shape of the spectrum did not change during this time. These facts indicate that TMPyP was intercalated into the clay film at a high density, which corresponds to an occupied area of 8.3 nm² per molecule, and the intercalation progressed without forming any aggregated species. We have reported that the strong host–guest interaction suppressed aggregation for 4+ charged cationic porphyrin molecules adsorbed on the surface of the monolayer SSA under the size-matching condition (Takagi et al., 2013). We suggest that this strong host–guest interaction was similarly effective during the intercalation process to suppress aggregated species.

The time profiles of the absorbance of the solution observed at 423.5 nm under the different temperature conditions are plotted in Fig. 5a and those of the TMPyP/SSA hybrid film observed at 580 nm are plotted in Fig. 5b. Figure 5c shows the superposition of the decay curves in Fig. 5a and the vertical inversion of the rise curves in Fig. 5b. The decrease of TMPyP in the solution was found to correspond to an increase in the intercalated species. When the temperature of the solution increased, the intercalation became faster.

The time profiles could be fitted well using an exponential-type function (Fig. 6a). The time rate constants \( k \) obtained by the fitting are \( 5.5 \times 10^{-5} \text{ s}^{-1} \) (292 K), 7.0 \( \times 10^{-5} \text{ s}^{-1} \) (298 K), 8.1 \( \times 10^{-5} \text{ s}^{-1} \) (303 K), and 1.2 \( \times 10^{-4} \text{ s}^{-1} \) (313 K). Figure 6b shows an Arrhenius plot of the rates. The plot is linear, and the activation energy is estimated to be 26.8 ± 0.6 kJ mol⁻¹.

DISCUSSION

According to the studies about the freeze-thaw intercalation (Takagi et al., 2002), the inverse process of intercalation was negligible because of the strong host–guest interaction. Therefore, a time course for the intercalation is simply described by

\[
dn_t/dt = -dn_t/dt = k' \times n_t
\]

where \( n_t \) and \( n_i \) denote the population of TMPyP in the immersion solution and that of TMPyP intercalated in SSA,
respectively; \( x \) denotes the fraction of the edge of the clay layered particles where the intercalation starts; and \( k' \) is a constant of proportionality. When \( x \) is constant, \( n_i \) and \( n_f \) follow an exponential time course with a rate \( k \) defined by \( k = k' x \). Note that the initial concentration of TMPyP molecule in the solution corresponds to 30% versus the CEC of the immersed clay film. If molecules stay at the entrance after intercalation, \( x \) decreases and the exponential time course is not maintained. Thus, it is presumed that molecules were drawn into the inside of the clay layers after the intercalation. As a result, \( x \) was maintained as a constant. Therefore, we think that this migration of TMPyP molecules in the clay layer did not limit the intercalation.

Two possible limiting processes are conceivable. Molecular diffusion is related to one of them. The SSA film was constructed from primary and/or secondary particles of layered clay sheets. TMPyP molecules are supplied to the surface of the film at all times because of stirring. The molecules need to diffuse in the space between the particles, from the surface to the edge of the primary particle before the intercalation. Interestingly, the activation energy of the intercalation rate constant is similar to that of the atomic ion diffusion (ECSJ, 1964). The value of the activation energy suggests that the intercalation process was controlled by this diffusion. On the other hand, the penetration of the molecules from the solute to the interlayer is also conceivable as the limiting process. We will validate this with various types of molecules (size, charge, rigidity, and so on).

Before this study, we hypothesized that there is a high activation energy caused by the steric hindrance of the TMPyP molecule because the size of the molecule was comparable to that of the interlayer space of the clay. We found that the
activation energy for the intercalation of a porphyrin-type molecule is not much higher than that of atomic ion diffusion, regardless of the limiting process. In future, we hope that artificial photosynthesis can be performed in clay layers with a light-harvesting system constructed with hybrids, including high density and aggregation-free dyes. We believe that substrates as large as porphyrin can access the reactants placed at the interlayer in such a case.

CONCLUSIONS

The intercalation process under the size-matching condition was studying using an immersion method. The intercalation generated a high density and aggregation-free hybrid of TMPyP and SSA. Population transfer from the solute in the interlayer on the intercalation followed a simple exponential time course with modest activation energy. No aggregated species were observed during the intercalation process. Various substrates, as large as a porphyrin molecule, can access the inside of the clay layer. These results make the fabricated hybrids useful for constructing many function materials as well as artificial photosynthesis devices.

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