Preparation of Langmuir–Blodgett films of aligned sepiolite fibers and orientation of methylene blue molecules adsorbed on the film†

Yasushi Umemura,*a Emi Shinoharaa and Robert A. Schoonheydtb

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Sepiolite is a clay mineral with a fibrous morphology; the fibers possess rectangular channels along the fiber direction, and have cation-exchange ability. Amphiphilic octadecylammonium cations (ODAH+) spread at an interface between the air and a dispersion of sepiolite fibers have hybridized with the fibers to form a floating monolayer. Surface pressure–molecular area isotherms did not indicate clear collapse points of the hybrid monolayers. Observation of the hybrid films on glass plates by atomic force microscopy revealed that the sepiolite fibers preferred to be aligned perpendicularly to the compression direction, and that some fibers overlapped upon compression or even before compression. Out-of-plane and in-plane X-ray diffraction patterns of the hybrid film showed that the fibers were not only aligned by the compression but oriented around the fiber direction. Electronic spectra of methylene blue cations (MB+) adsorbed on the hybrid film indicated the presence of monomers and dimers of MB+. The absorption intensity due to the monomer was dependent on the polarization direction of the incident beam; interestingly, the monomers were spontaneously oriented along the sepiolite fiber direction but the dimers were not oriented. By comparison with the results of rhodamine 6G adsorbed on the film, the monomers of MB+ would probably be present in the channels of sepiolite fibers, while the dimers would be adsorbed on the external surface of the fibers.

Introduction

The Langmuir technique for the preparation of ultrathin films has been applied not only to amphiphilic molecules, but also to various nanomaterials. The nanomaterial particles stabilized with a surfactant are spread onto an air–water interface and compressed by barriers of a Langmuir trough to form a close-packed floating film (Langmuir film).1–10 One of the attractive properties of Langmuir films of nanowires and nanorods is anisotropic alignment of the nanomaterials controlled by the compression direction and the surface pressure.4–10

In the application of films to sensing and catalysis, it is desirable to employ porous materials as film components to maximize the number of molecules interacting with the films. Unfortunately, the nanowires and nanorods themselves used so far in the aligned Langmuir films are not porous.4–10 Carbon nanotubes possess one-dimensional channel structures and they can include molecules such as H2O and fullerenes in their channels.11,12 Langmuir or Langmuir–Blodgett (LB) films of carbon nanotubes13–18 have been reported. However, adsorption and desorption of molecules is difficult, because, in general, the ends of the channels are closed.11 Zeolites are well-known as microporous materials, and zeolite films with a one-dimensional channel structure have been synthesized,19–22 but the direction of these channels was perpendicular to the film surface, not parallel to the surface. Recently, LB films of imogolite (a clay mineral with a hollow tube structure) were reported.23 However, the adsorption properties of molecules onto the films were not mentioned.

Sepiolite is a clay mineral (hydrated magnesium silicate) with a fibrous morphology.24–27 The dimensions of the fibers vary widely, but are generally 0.2–2 μm in length and (10–30) × (5–10) nm in cross section. The unit cell parameters are a = 1.33 nm, b = 2.695 nm, c = 0.528 nm, and β = 90°. The c-axis is parallel to the fiber direction. The surface area of sepiolite is high (200–500 m2 g−1), because it possesses rectangular channels (1.06 × 0.37 nm) along the fiber direction (Fig. 1). Sepiolite shows cation-exchange ability. Due to these properties, sepiolite has been used as adsorbent and catalyst.28 Films of sepiolite were studied for applications in optical and electrical devices.27,28 However, the alignment of the sepiolite fibers in those films was random within the film plane. If the fibers are aligned in the film plane, one can expect that molecules adsorbed in the channels will be spontaneously ordered along the alignment of the fibers. This orientation of the molecules in the film plane may bring about interesting applications in e.g. sensors and optical polarizers.

We have studied Langmuir films of inorganic nanosheets (smectite clay minerals and layered titanias) and amphiphilic organic compounds.30–35 In the case of the smectite clay, for example, the stacked layers of the clay are exfoliated into single clay nanosheets (1 nm thick and negatively charged) in

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a Department of Applied Chemistry, National Defense Academy, Hashirimizu 1-10-20, Yokosuka, Kanagawa 223-8686, Japan. E-mail: umemura@nda.ac.jp; Fax: +81-46-844-5901
b Centre for Surface Science and Catalysis, K.U.Leuven, Kasteelpark Arenberg 23, B-3001 Leuven, Belgium. E-mail: Robert.Schoonheydt@biw.kuleuven.be

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an aqueous dispersion at a low concentration. When amphiphilic organic cations were spread onto an air–water interface of the dispersion of the smectite clay nanosheets, the negatively charged nanosheets were adsorbed onto the floating monolayer of the amphiphilic cation. These organic/inorganic hybrid particles floating at the interface were gathered by compression of the barriers to form a close-packed film. Despite the anisotropic compression, the orientation of the clay nanosheets in the hybrid film is random because of their irregular shapes.36

In this work, sepiolite fibers have been employed instead of inorganic nanosheets. By anisotropic compression, we expected the sepiolite fibers to be aligned in the film plane (Fig. 2) though the size irregularity of the fibers might cause some disturbance of the alignment. If the size of a molecule fits the rectangular shape of the sepiolite channel, it is expected that the molecule will penetrate into the channel and that its molecular orientation will be fixed according to the fiber direction in the hybrid film. In order to confirm this expectation, cationic dyes of methylene blue (MB+)37–40 and rhodamine 6G (R6G+)41 were adsorbed on the sepiolite films and the orientation of the dye molecules was investigated.

Experimental section

Sepiolite used in this work was PANGEL AD from TOLSA, S. A., Spain (surface area 320 m² g⁻¹; cation-exchange capacity (CEC) 0.10–0.15 mequiv. g⁻¹; catalog data). The clay (0.2 g) was suspended in 1 dm³ of water (~0.05 µS), and one day later the dispersion was ultrasonicated for 1 h. The sepiolite dispersion prepared in this way was used as a stock dispersion at a concentration of 200 ppm (mg dm⁻³). The sepiolite fibers were dispersed (no precipitate was observed) for several days. This stock dispersion was diluted with water to a given concentration just prior to use. An amphiphilic salt of octadecylammonium chloride (CH₃(CH₂)₁₇NH₃+Cl⁻: ODAH⁺Cl⁻) was dissolved in a mixed solvent of chloroform and methanol (4:1 in volume) at 2 × 10⁻⁴ mol dm⁻³. The solution of ODAH⁺Cl⁻ was spread onto the surface of the sepiolite dispersion in a Langmuir trough (KSV Minitrough) after impurities on the surface were removed by suction. After 15 min, a surface pressure–molecular area (π–A) isotherm curve was measured by compressing the floating film from the both sides with barriers. The change in surface pressure upon the compression was monitored by the Wilhelmy method using a Pt plate.

For atomic force microscopic (AFM) observation and X-ray diffraction (XRD) measurements, the floating films were transferred onto glass plates by horizontal dipping, and then the film surfaces were rinsed with water several times. The AFM observation of the films was carried out by a PicoPlus apparatus (Molecular Imaging, USA) in a TopMAC mode. XRD patterns of the films were obtained with X’Pert MRD (PANalytical B. V., the Netherlands) using the Cu Kα₁ line.

Dye cations of MB⁺ and R6G⁺ were adsorbed on the sepiolite films transferred on glass plates at a surface pressure of 40 mN m⁻¹ from a 20-ppm dispersion. A drop of an aqueous dye (chloride) solution (1.0 × 10⁻³ mol dm⁻³) was put on the film surface for 1 day at room temperature. After the film surface was washed with water, electronic spectra (in a transmission mode) of the dye adsorbed on the film were recorded with plane-polarized beams in the visible region by using the spectrophotometer U-3310 (Hitachi, Japan). A glass plate was used as a reference sample.

Results and discussion

Packing structure of hybrid films

Before the preparation of the hybrid films, the surfaces of the sepiolite dispersions in the LB trough were cleaned. Fig. 3a shows the change in surface pressure when the surface area (20-ppm sepiolite dispersion) was reduced by compression with the barriers. The rise in surface pressure by the compression was less than 1 mN m⁻¹. The surface of the dispersion is clean enough for the film preparation.

The π–A isotherm curve for ODAH⁺ spread on a sepiolite dispersion at 20 ppm is shown in Fig. 3b. The abscissa indicates molecular area; a calculated area per ODAH⁺ cation. As the floating film of ODAH⁺ is compressed, the surface pressure starts to rise from ~0.4 nm² molecule⁻¹. The π–A isotherm curve of ODAH⁺ on water (Fig. 3b) indicates...
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of the ODAH + cations on the surface would be dissolved into

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sectional area of the alkyl chains,

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a surface pressure of 63 mN m

\[ 1 \]

the onset of surface pressure at \( \sim 0.3 \text{ nm}^2 \text{ molecule}^{-1} \)

and the collapse of the floating monolayer at \( \sim 0.13 \text{ nm}^2 \text{ molecule}^{-1} \) at a surface pressure of 63 mN m

\[ 1 \]. (Considering the cross-sectional area of the alkyl chains, \( \sim 0.19 \text{ nm}^2 \), the molecular area of \( \sim 0.13 \text{ nm}^2 \) is too small. The monolayer of ODAH + on water around pH \( \sim 5.6 \) is probably unstable, \( 42,43 \) so that some of the ODAH + cations on the surface would be dissolved into water by the compression.) The onset of surface pressure for the film on the sepiolite dispersion is different from that on water, and no collapse point is observed on the isotherm curve of the film on the dispersion. These differences suggest the hybridization of ODAH + and sepiolite fibers at the interface. The features on the \( \pi-A \) isotherm curve of ODAH + on the sepiolite dispersion also differ from those on a clay nanosheet dispersion. On a 20-ppm dispersion of montmorillonite, one of the smectite clay minerals, the \( \pi-A \) isotherm curve (Fig. 3b) gives the large area at the onset of surface pressure \( \sim 1.3 \text{ nm}^2 \text{ molecule}^{-1} \) and the collapse point at \( \sim 0.7 \text{ nm}^2 \text{ molecule}^{-1} \) (40 mN m

\[ 1 \]).

\[ \pi-A \] Isotherm curves of ODAH + monolayers on the sepiolite dispersions at 20, 50, 100 and 200 ppm are shown in Fig. 4. The isotherm curves shift to the smaller molecular-area side with the decrease of the sepiolite concentration in the dispersion. This dependence of the isotherm on the sepiolite concentration also suggests hybridization of ODAH + cations and sepiolite fibers at the air–dispersion interface.

No collapse points are observable on these isotherm curves in Fig. 4. This feature of the sepiolite film will be discussed on the basis of AFM data below.

In order to investigate the packing of the floating hybrid films as a function of surface pressure, the films formed on the surface of the 20-ppm dispersion were transferred onto glass plates at surface pressures of 0 (before compression), 20 and 40 mN m

\[ 1 \], and their packing structures were observed by AFM. The AFM image of the film deposited before compression (Fig. 5a) shows fibrous particles of sepiolite (hybridized with ODAH +: sepiolite/ODAH +) with various sizes; the width ranges from 50 to 150 nm and the thickness from 10 to 15 nm. The particles seem to prefer such an orientation that both the \( c \)-axis direction and the longer side in the cross section (\( b \)-axis direction) are parallel to the surface (Fig. 1). \( 27 \) The particles are isolated from each other, but some of them overlap, even before the compression. Alignment of the fibers (orientation along the fiber-direction) is random. At 20 mN m

\[ 1 \] compression (Fig. 5b), the particles are touching each other and many particles overlap. They tend to be aligned perpendicularly to the direction of the applied compression. However, some empty spaces remain between the particles. On further compression (40 mN m

\[ 1 \], Fig. 5c), the whole surface of the film is covered with the sepiolite particles and most of them are aligned.

Generally, a collapse point appears in a \( \pi-A \) isotherm curve when a floating single-layer film is broken by compression to form a double- or triple-layer film. \( 44-46 \) The AFM observation of the sepiolite/ODAH + film reveals that some sepiolite particles overlap even before the compression (Fig. 5a). It is likely that the long fibrous particles of sepiolite become entangled with one another when they are adsorbed onto the floating monolayer of ODAH + at the air–dispersion interface. The AFM images also indicate that the particles overlap easily with compression (Fig. 5b and 5c). It is probable that the irregularities in thickness and edge-shapes of the sepiolite particles cause overlapping of the neighboring particles at low surface pressures. As can be seen in the AFM images in Fig. 5b and 5c, this overlapping increases with the rise in the surface pressure. Such overlapping of the floating sepiolite/ODAH + fibers would result in the disappearance of the collapse point in the \( \pi-A \) isotherm curves.
The powder XRD pattern of sepiolite is shown in Fig. 6a. The peak assignment is done according to the literature. The diffraction peak at $2\theta = 7.3^\circ$, assigned to (110), is much more intense than the other peaks. The out-of-plane XRD pattern (Fig. 7a) for the hybrid film of sepiolite/ODAH + transferred onto a glass plate at 40 mN m$^{-1}$ (from the 20-ppm dispersion interface) is shown in Fig. 6b. If most of the sepiolite particles are oriented with the $b$- and $c$-axes parallel to the film surface (Fig. 8), the $(h00)$ diffraction lines should be observable in the out-of-plane XRD pattern. Truly, the (400) diffraction peak at $2\theta = 27^\circ$ is observed on the halo of the glass substrate in Fig. 6b. The (200) peak around $2\theta = 13^\circ$ is too weak to be detected. The (110) diffraction line appears as a weak peak at $2\theta = 7.3^\circ$. Many of the particles overlap in the film as observed in the AFM image (Fig. 5c). This disturbance of the fiber alignment could cause the appearance of the weak (110) diffraction. Fig. 6c shows the in-plane XRD pattern of the hybrid film. The sample was placed such that the compression direction bisects the angle between the incident and diffracted beams (Fig. 7b). In this geometry the $(0k0)$ diffraction is detectable, if the sepiolite fibers are oriented with their $b$- and $c$-axes parallel to the film surface (Fig. 8). Actually the in-plane XRD pattern (Fig. 6c) indicates a peak at $2\theta = 19.7^\circ$, which is assigned to the (060) diffraction. Thus, these XRD results, taken together, reveal that the sepiolite fibers in the films prepared by the Langmuir method are not only aligned perpendicularly to the compression direction, but are oriented with their $b$- and $c$-axes parallel to the film surface, though some deviations occur.

**Orientation of sepiolite fibers around the fiber direction**

The powder XRD pattern of sepiolite is shown in Fig. 6a. The peak assignment is done according to the literature. The diffraction peak at $2\theta = 7.3^\circ$, assigned to (110), is much more intense than the other peaks. The out-of-plane XRD pattern (Fig. 7a) for the hybrid film of sepiolite/ODAH + transferred onto a glass plate at 40 mN m$^{-1}$ (from the 20-ppm dispersion interface) is shown in Fig. 6b. If most of the sepiolite particles are oriented with the $b$- and $c$-axes parallel to the film surface (Fig. 8), the $(h00)$ diffraction lines should be observable in the out-of-plane XRD pattern. Truly, the (400) diffraction peak at $2\theta = 27^\circ$ is observed on the halo of the glass substrate in Fig. 6b. The (200) peak around $2\theta = 13^\circ$ is too weak to be detected. The (110) diffraction line appears as a weak peak at $2\theta = 7.3^\circ$. Many of the particles overlap in the film as observed in the AFM image (Fig. 5c). This disturbance of the fiber alignment could cause the appearance of the weak (110) diffraction. Fig. 6c shows the in-plane XRD pattern of the hybrid film. The sample was placed such that the compression direction bisects the angle between the incident and diffracted beams (Fig. 7b). In this geometry the $(0k0)$ diffraction is detectable, if the sepiolite fibers are oriented with their $b$- and $c$-axes parallel to the film surface (Fig. 8). Actually the in-plane XRD pattern (Fig. 6c) indicates a peak at $2\theta = 19.7^\circ$, which is assigned to the (060) diffraction. Thus, these XRD results, taken together, reveal that the sepiolite fibers in the films prepared by the Langmuir method are not only aligned perpendicularly to the compression direction, but are oriented with their $b$- and $c$-axes parallel to the film surface, though some deviations occur.

### Spontaneous orientation of adsorbed MB$^+$

Powder XRD patterns of sepiolite samples on which MB$^+$ and R6G$^+$ (Fig. 9) were adsorbed (see ESI†) are shown in
Fig. 10, together with the XRD patterns of the original sepiolite (without the dye adsorption, the same sample as Fig. 6a) and polycrystalline MB\(^+\) (chloride) for comparison. Although the XRD pattern of the MB\(^+\)-adsorbed sepiolite (Fig. 10b) resembles that of the original sepiolite (Fig. 10a), the relative intensity of the (400) peak at 2\(\theta\) = 26.7\(^\circ\) is larger than that of the original sepiolite. The intensity ratios of (400)/(110) are 0.25 for the original sepiolite and 0.41 for the MB\(^+\)-adsorbed sepiolite. The XRD pattern of polycrystalline MB\(^+\) (chloride, Fig. 10d) gives intense peaks at 2\(\theta\) = 25.6 and 26.2\(^\circ\) near the (400) peak of the sepiolite. However, in the pattern of MB\(^+\)-adsorbed sepiolite, the contribution of these peaks (due to polycrystalline MB\(^+\)) to the (400) peak is negligible, because there is no peak at 2\(\theta\) = 9.2\(^\circ\), where another strong peak is observed in the pattern of polycrystalline MB\(^+\). The XRD pattern of R6G\(^+\)-adsorbed sepiolite (Fig. 10c) is almost the same as that of the original sepiolite (Fig. 10a). The (400)/(110) ratio is 0.27, which is close to the value for the original sepiolite (0.25).

Therefore, these XRD results suggest that the MB\(^+\) cation should be present in the channel of sepiolite in regular order (see ESI\(^*\)). Since the size of MB\(^+\) is \(\approx 0.33 \times 0.76 \times 1.70\) nm\(^2\) (Fig. 9a), MB\(^+\) could enter the channel of sepiolite with the long axis of MB\(^+\) parallel to the fiber direction (c-axis). On the other hand, the R6G\(^+\) cation, the size of which is larger than the size of the channel, would be adsorbed on the external surface of sepiolite.

Electronic spectra of MB\(^+\) adsorbed on the sepiolite/ODAH\(^+\) film were measured with polarized beams: the planes of polarization (electric field) were parallel and perpendicular to the compression direction of the sample (Fig. 11). The polarized spectra of MB\(^+\) adsorbed on sepiolite/ODAH\(^+\) are given in Fig. 12a and 12b. Both spectra show absorption peaks at 605 and 655 nm due to the dimer (H-type) and monomer of MB\(^+\), respectively.\(^{49-59}\) The absorption intensities of these bands measured with the beam polarized perpendicularly to the compression direction (the polarized plane nearly parallel to the fiber direction, Fig. 11a) are more intense than those measured with the beam polarized parallel to the compression direction (the polarized plane nearly perpendicular to the fiber direction, Fig. 11b). This suggests that the MB\(^+\) cations adsorbed on the film are oriented spontaneously. To compare the spectrum measured by the beam polarized perpendicularly to the compression direction (Fig. 12a) with that measured by the beam polarized parallel to it (Fig. 12b), the former spectrum was subtracted by the latter (Fig. 12a – Fig. 12b) as shown in Fig. 12c. This subtraction spectrum is dominated by the monomer band at 655 nm. Thus, the monomer spectrum is strongly affected by the change in polarization, while the dimer absorption is not. (see ESI\(^*\))

These absorptions (605 and 655 nm) are associated with the transition moment along the long axis of MB\(^+\).\(^{51}\) Therefore, the differences in the absorption intensities between the polarized spectra imply that the monomers of MB\(^+\) are preferentially oriented with their long axes parallel to the fiber direction.\(^{60}\) It is likely that the monomeric MB\(^+\) cations are adsorbed in the channels of the sepiolite fibers.

The absorption at 605 nm is indicative of the existence of the MB\(^+\) dimers. It is impossible for the dimer to enter the channels of the sepiolite fibers because of its large size. The dimer of MB\(^+\) can be adsorbed on the external surface of the fiber, leading to a nearly random orientation. Hence, only a little change in the peak intensity at 605 nm is observed between the two spectra measured with the polarized beams.

There remains the possibility that the monomers of MB\(^+\) might be adsorbed on the external surface of the sepiolite fibers in the film and that they might be oriented according to the grooves or cracks on the external surface, which run parallel to the fiber direction. In order to confirm the above-mentioned interpretation that the monomeric MB\(^+\) molecules enter the sepiolite channels, R6G\(^+\) was adsorbed on the
hybrid film. The size of R6G+ (Fig. 9b) is too large to enter the channel of sepiolite. Fig. 13a and 13b show the electronic spectra of R6G+ adsorbed on the sepiolite/ODAH+ film measured with the beams polarized perpendicularly and parallel to the compression direction, respectively. The absorption peak at 526 nm and the weak absorption as a shoulder at 500 nm are observable; they are assigned to the monomer and dimer of R6G+, respectively. There is a little difference between these spectra. The subtraction spectrum of the polarized spectra is shown as Fig. 13c. This means that the absorption at 526 nm in the spectrum measured with the perpendicularly polarized beam is a little larger than the corresponding absorption in the spectrum measured with the parallel polarized beam, and that there is no difference in the absorption intensities for the shoulder at 500 nm.

Conclusions

Hybrid films of sepiolite fibers and amphiphilic alkyl-ammonium cations were prepared by the Langmuir method. The fibers in the hybrid film were aligned perpendicularly to the compression direction, although some fibers were out of order and some were overlapping. Such disorder would be caused by the shape irregularities of the sepiolite fibers.

The monomers of MB+ adsorbed on the hybrid film were oriented with their long axes perpendicular to the compression direction of the film, but the dimers were not. Most of the monomers would probably be located in the channels of the sepiolite fibers. This is a good example of spontaneous ordering of molecules in the channels of sepiolite fibers.

The XRD results for the films (Fig. 6) reveal that the sepiolite fibers are oriented around the c-axis (fiber direction) with the b- and c-axes parallel to the film surface. Therefore, it can be expected that MB+ cations in the channel of the sepiolite fibers should be oriented with the molecular plane of MB+ parallel to the film surface (in addition to the orientation of the long axis of MB+), though we have failed to obtain any information on the orientation of the molecular plane so far (by infrared spectroscopy, for example).

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References

45. The alignment of the fibers in the sepiolite/ODAH + film deposited at 40 mN m⁻¹ is disturbed to some extent (Fig. 5c). This disturbance may give rise to the residual absorption at 655 nm in the spectrum measured with the light polarized parallel to the compression direction.