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# Structure of a layered octosilicate intercalated with alkylamines with different molecular structures in water

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## Abstract

A comparative study to experimentally examine the effects of the guest molecular structure on the intercalated structure of a host layered material was systematically performed, aiming to control the structure of organosilicates. Layered octosilicate with hydrogen ions in the silicate interlayers (H-octosilicate) as the host was intercalated with water-insoluble guest alkylamines with different molecular structures, e.g., primary *n*-alkylamines with different alkyl chain lengths and secondary and tertiary dodecylamines with different numbers of dodecyl chains and methyl groups, in water by a simple method that we newly developed. The primary *n*-alkylamine-intercalated compounds had well-ordered structures with alkylamine bilayers in the interlayer space. The interlayer distances were relatively large compared with the quaternary ammonium ion-intercalated ones. Using the primary, secondary and tertiary dodecylamines, the structure of intercalated compounds drastically changed depending on the type of hydrocarbon group and the number of hydrogen atoms bonded to the nitrogen atom of the amine. The primary *n*-alkylamine-intercalated compounds showed good adsorption properties of methyl orange in water, which suggested that the intercalated compounds are promising candidates for removal of anionic dyes.

## Keywords

Alkylamine, Intercalation, Layered octosilicate, Ordered structure

## 1. Introduction

Organically modified layered silicates (called organosilicate or organoclay), which are a type of organic-inorganic hybrid materials, have been actively studied as functional materials in various fields [1–3]. In particular, organosilicates with well-organized nanostructures, which are synthesized by intercalating guest organic molecules/ions into the interlayer space of host layered silicates, have attracted much attention as fillers in polymer-clay nanocomposites with high performances [4, 5]. Although various layered silicates and clay minerals are used as the host material, layered alkali octosilicate [6, 7], which is a layered polysilicate, is a promising candidate because it has a regular rectangular morphology and the size-controlled platelets can be synthesized [8]. Several studies on the intercalation of octosilicate with various guests such as alkylamine molecules and alkylammonium ions have been reported [9–15], which indicates that the structure of intercalated compounds depends on the guest molecule/ion structure.

In practical applications of the intercalated compounds, their structure plays an important role. For example, when intercalated compounds are used as fillers in the polymer-clay nanocomposites, they must be uniformly dispersed in the polymer matrix. In addition, many cases require to exfoliate the intercalated compounds to individual thin platelets with nanometer-sized thicknesses, i.e., nanosheets [13,15]. The dispersion and exfoliation of intercalated compounds can be affected by their structure and surface conditions. Thus, to synthesize polymer-clay nanocomposites with the desired properties and performance, intercalated compounds with controlled structures suitable for the designed nanocomposites are required. Therefore, it is of great importance to precisely control the structure of intercalated compounds. However, to the best of our knowledge, no study systematically investigated the effects of guest molecules/ions on the intercalated structure. Accordingly, it is still challenging to obtain intercalated octosilicate with controlled structures.

This study aims to control the structure of layered octosilicate by the intercalation of various guest molecules. Therefore, a comparative study to examine the effects of guest molecular structure on the intercalated structure of octosilicate was performed. For the intercalation of guest molecules, our new simple method, which can produce water-insoluble alkylamine-intercalated octosilicate with a well-ordered structure in water [16] was used as an alternative of a widely employed conventional method to intercalate quaternary ammonium ions into octosilicate by ion exchange. The effects of structure and intercalated amount of guest alkylamine molecules on the structure of resulting compounds were studied through the systematic experiments. Furthermore, as a potential application of the organosilicates, the adsorption of anionic dye (methyl orange) [17–21] on the intercalated compounds was examined.

## 2. Experimental

The alkylamines in this work were purchased from Tokyo Chemical Industry and used without further purification. Table 1 lists the melting point and water solubility of alkylamines. Primary alkylamines with a *n*-alkyl chain with 6–18 carbon atoms and secondary and tertiary dodecylamines with different numbers of *n*-dodecyl chains and methyl groups were used as the guest molecule to intercalate the host octosilicate. A sodium silicate solution to synthesize layered octosilicate, which consisted of 23.44 mass% SiO<sub>2</sub> and 6.29 mass% Na<sub>2</sub>O, was supplied from Nippon Chemical Industrial.

**Table 1**

Alkylamines with different molecular structures in this work.

Guest amine	Formula	Class of amine	Symbol	Melting point [°C]	Water solubility
Hexylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> NH <sub>2</sub>	Primary	C6	-23	Soluble (12 g/L)
Octylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> NH <sub>2</sub>	Primary	C8	-1	Slightly soluble (0.2 g/L)
Decylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> NH <sub>2</sub>	Primary	C10	13	Insoluble
Dodecylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> NH <sub>2</sub>	Primary	C12	26	Insoluble
Tetradecylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> NH <sub>2</sub>	Primary	C14	37	Insoluble
Hexadecylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> NH <sub>2</sub>	Primary	C16	44	Insoluble
Octadecylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> NH <sub>2</sub>	Primary	C18	53	Insoluble
<i>N</i> -Methyldodecylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> NHCH <sub>3</sub>	Secondary	C12-C	20	Insoluble
<i>N,N</i> -Dimethyldodecylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> N(CH <sub>3</sub> ) <sub>2</sub>	Tertiary	C12-2C	-20	Insoluble
Didodecylamine	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> ] <sub>2</sub> NH	Secondary	2C12	51	Insoluble
<i>N,N</i> -Didodecylmethylamine	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> ] <sub>2</sub> NCH <sub>3</sub>	Tertiary	2C12-C	16	Insoluble
Tridodecylamine	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> ] <sub>3</sub> N	Tertiary	3C12	16	Insoluble

Octosilicate with Na<sup>+</sup> ions in the interlayers (denoted as Na-octosilicate) was synthesized by the hydrothermal treatment of the sodium silicate solution at 110°C for 12 days without seed crystals [8]. The interlayer Na<sup>+</sup> ions of Na-octosilicate obtained were ion-exchanged with H<sup>+</sup> ions by soaking Na-octosilicate twice in 0.1 mol/L hydrochloric acid solution [22]. The resulting protonated octosilicate (denoted as H-octosilicate) was obtained by washing the precipitate with deionized water several times, followed by drying at 80°C in air under atmospheric pressure.

One hundred milligrams of H-octosilicate was added to 20 mL of deionized water, and the H-octosilicate aggregates were disintegrated using an ultrasonic bath (38 kHz, 400 W) for few minutes. Subsequently, 0.77 mmol of an alkylamine was added to the suspension. The dose of alkylamine was theoretically determined, assuming that the chemical formula of H-octosilicate is expressed as Si<sub>4</sub>O<sub>7</sub>(OH)<sub>2</sub> [23] and the amino groups of alkylamine adequately bond to the hydroxyl groups in the surface and interlayer of H-octosilicate [22]. Thus, the molar ratio of nitrogen atom (N) in alkylamine to hydroxyl group (OH) in H-octosilicate was 1 in this case. To insert the alkylamine molecules into the interlayer space of H-octosilicate, the alkylamine-containing suspension was vigorously stirred for 30 min at room temperature (approx. 28°C) when the melting point of alkylamine was lower than room temperature. For alkylamines with a melting point above room temperature, i.e., C14, C16, C18 and 2C12, the suspension was heated at 10 degrees higher than its melting point (for example, 47°C for C14) before stirring to completely melt the alkylamine. In addition, for C10 and C18, the N/OH molar ratio was varied from 0.2 to 1.2. After the intercalation treatment, the suspension was filtered, and the separated precipitate was dried at room temperature overnight.

The structure of the samples was confirmed by a powder X-ray diffractometer (XRD-6100, Shimadzu; CuKα, λ = 0.15418 nm, 30 mA, 30 kV, 1°/min). The thermogravimetry/differential thermogravimetric analysis (TG/DTA) was conducted by a thermogravimetric analyzer (DTG-60, Shimadzu) to determine the content and thermal decomposition temperatures of alkylamines in the intercalated compounds. The alkylamine contents were calculated using the weight loss from 130°C to 700°C. In the evaluation of methyl orange (MO) removal by

adsorption using the intercalated compounds as the adsorbent, 40 mg of a sample powder was added to 20 mL of 20 mg/L MO solution [17] and vigorously mixed for 5 min at room temperature. The absorbance of the filtered solution was measured at 464 nm using a spectrophotometer (U-2900, Hitachi) to determine the MO removal defined by

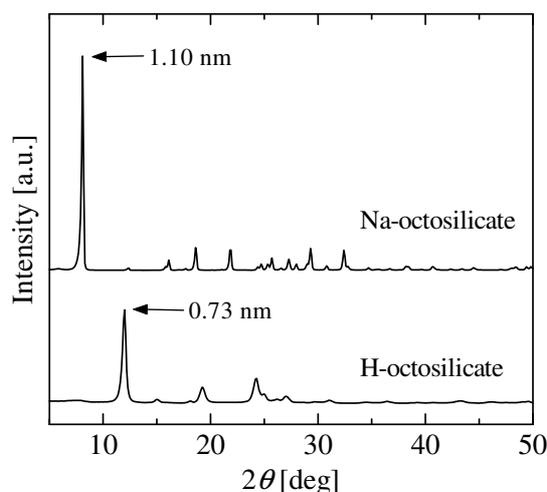
$$\text{MO removal [\%]} = [1 - (C/C_0)] \times 100 \quad (1)$$

where  $C_0$  and  $C$  are the concentrations of MO in the solution before and after the adsorption, respectively.

### 3. Results and Discussion

#### 3.1. Intercalation with primary *n*-alkylamines

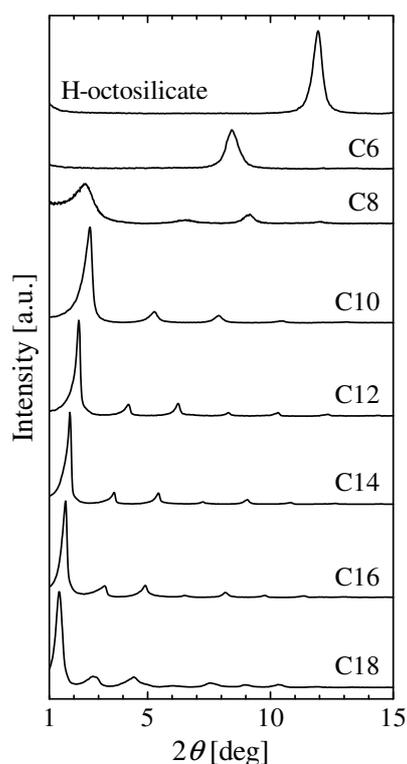
Fig. 1 shows the XRD pattern of Na- and H-octosilicate. Na-octosilicate has a basal spacing of 1.10 nm, and the protonation decreased the basal spacing to 0.73 nm. The crystal structure of Na-octosilicate has been analyzed in detail by some research groups; Vortmann et al. [24] proposed a possible model for the structure of RUB-18 (which is considered to be identical to Na-octosilicate) that the silicate layer is built up of the basic unit which is made of four five-membered rings containing eight  $\text{SiO}_4$  tetrahedra. According to the structure, they also determined the chemical formula of  $\text{Na}_8[\text{Si}_{32}\text{O}_{64}(\text{OH})_8] \cdot 32\text{H}_2\text{O}$ .



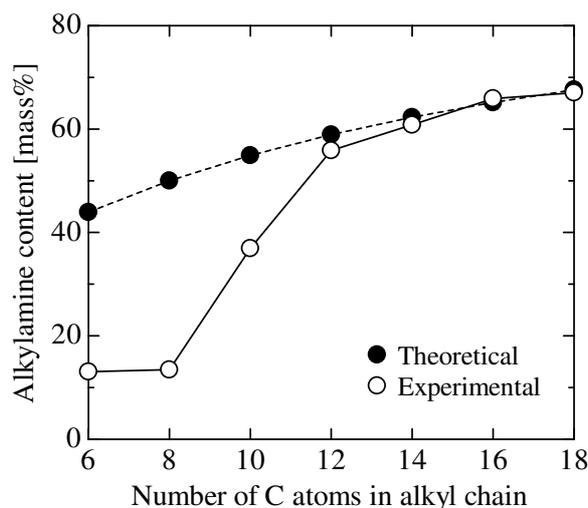
**Fig. 1.** XRD pattern of Na- and H-octosilicate.

Fig. 2 shows the XRD pattern of compounds intercalated with primary *n*-alkylamines at a N/OH molar ratio of 1. When C6 with relatively high water solubility was used, the basal spacing of the intercalated compound was slightly increased from that of H-octosilicate. The use of C8, which barely dissolves in water, resulted in the formation of the intercalated compound with a larger basal spacing and a disordered structure. In contrast, when primary amines with an alkyl chain whose number of carbon atoms is 10–18 were used, the structure of intercalated compounds was well ordered, and the basal spacing greatly increased because the intercalation with water-insoluble alkylamines in water can produce intercalated compounds with large basal spacings and well-ordered structures [16]. Fig. 3 depicts the alkylamine content

of the intercalated compounds together with the theoretical values. The C6- and C8-intercalated compounds had relatively low alkylamine contents; however, when using longer alkylamines, large amounts of alkylamines were intercalated. In particular, for the C12–C18-intercalated compounds, the actual alkylamine contents almost coincided with the theoretical values, which can contribute to formation of the well-ordered structures. The DTA results (data not shown) confirmed that no endothermic peaks were obtained at the melting point of corresponding alkylamines for the C14-, C16-, C18- and 2C12-intercalated compounds, suggesting that no free alkylamine molecules existed in the outside of H-octosilicate. In addition, the thermal decomposition temperatures of C6–C18 for the intercalated compounds were between 355°C and 450°C, which were higher than the evaporation and thermal decomposition temperatures of corresponding pure alkylamines; for example, C6 in the intercalated compounds was decomposed at 450°C although pure C6 was evaporated at temperatures higher than approximately 120°C. The results imply that the thermal stability of alkylamines is enhanced in the intercalated compounds. To further investigate the thermal stability of the intercalated compounds, as an example, the C18-intercalated compound was calcined at 600°C in air for 1 h. The XRD analysis of the calcined sample (data not shown) confirmed that it was amorphized during the calcination, indicating that the original layered structure of H-octosilicate was lost after removal of the alkylamine molecules from the interspaces.



**Fig. 2.** XRD pattern of compounds intercalated with primary alkylamine with different alkyl chain lengths.

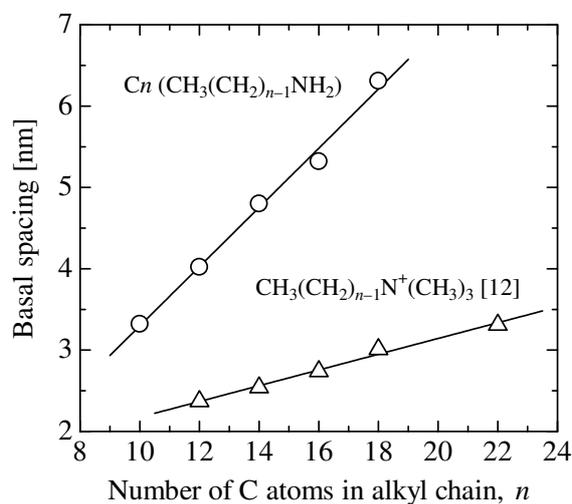


**Fig. 3.** Content of primary alkylamines in the intercalated compounds.

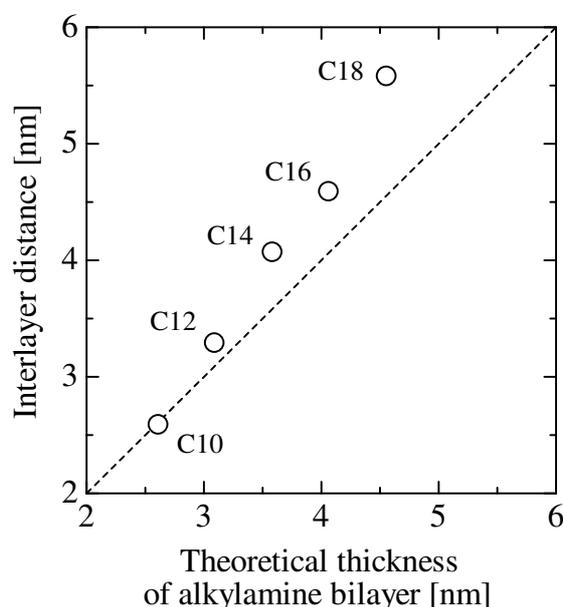
The intercalation of layered silicates with long-chain alkylamines may provide inorganic-organic compounds with MCM-41 type structure [25,26]. If our intercalated compounds have MCM-41 type structure, clear four XRD peaks at low angles corresponding to the (100), (110), (200) and (210) planes of MCM-41 can be obtained [25] and the ratio of basal spacings ( $d$ -values) of the reflections can be 1:0.577:0.5:0.378 [27]. However, as shown in Fig. 1, our samples with C10–C18 had clear three XRD peaks at angles lower than  $8^\circ$  and the ratios of  $d$ -values for the samples were not coincided with that for MCM-41. In addition, the  $d$ -values calculated using the three XRD peaks almost followed the correlation  $d, d/2, d/3$  for each intercalated compound, indicating that the three XRD peaks correspond to the (001), (002) and (003) planes of intercalated layered silicates, respectively [28]. The results suggest that the C10–C18-intercalated compounds have a lamellar (bilayer) structure, which is similar to the cases of intercalation of Na-octosilicate with quaternary alkyl ammonium ions [29].

Fig. 4 shows the relationship between the basal spacing of compounds intercalated with C10–C18 and the number of carbon atoms in the alkyl chain and compounds intercalated with quaternary ammonium ions, which consist of one  $n$ -alkyl chain and three methyl groups [12]. The basal spacing of our samples linearly increased with increasing number of carbon atoms and was much larger than that of the ammonium ion-intercalated compounds. When quaternary ammonium salts were used, the ammonium ions were solvated by water molecules, which could affect the arrangement of ammonium ions in the interlayer space. In addition, the TG analysis confirmed that our samples had higher alkylamine contents compared with the corresponding quaternary ammonium ions-intercalated compounds: e.g., the hexadecyltrimethylammonium ions- and trimethylstearylammonium ions-intercalated ones had an ammonium ion content of 42.3 and 53.0 mass%, respectively. The results suggest that the use of guest-insoluble solvents effectively contributes to the expansion of the interlayer distance. Fig. 5 shows a comparison of the interlayer distance of our samples with the theoretical thickness of bilayer consisting of each alkylamine molecule. The theoretical bilayer thickness was determined as twice the length

of corresponding alkylamine molecule, which was computed using a quantum chemical calculation software (Firefly version 8.2.0). The experimental interlayer distance was almost consistent with the theoretical thickness of the alkylamine bilayer. However, at larger alkyl chain lengths, the experimental data were larger than the calculated values, which suggests that some free alkylamine molecules lay in the alkylamine bilayer.



**Fig. 4.** Relationship between basal spacing of alkylamine-intercalated compounds and number of carbon atoms in the alkyl chain.

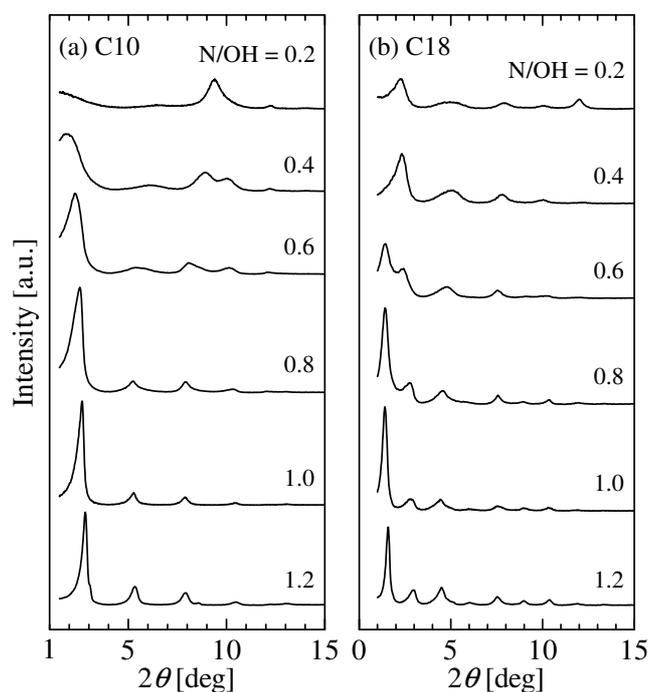


**Fig. 5.** Relationship between the interlayer distance of primary alkylamine-intercalated compounds and the theoretical thickness of the alkylamine bilayer.

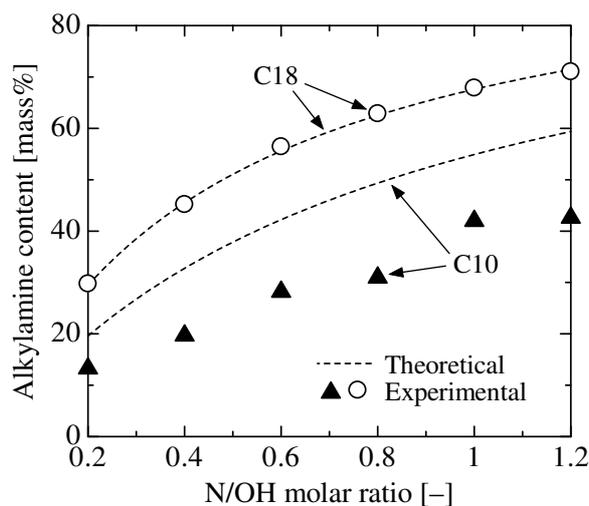
### 3.2. Effect of the dosage and class of alkylamine

Fig. 6 shows the XRD pattern of compounds intercalated with C10 and C18 at various N/OH molar ratios. In both C10- and C18-intercalated compounds, their structure became more

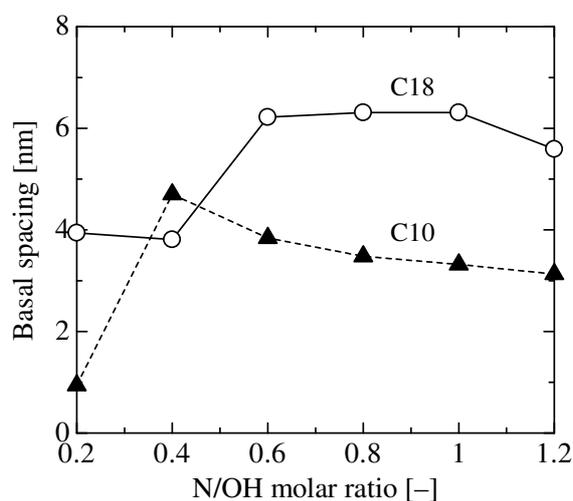
ordered with increasing N/OH molar ratio. The changes in the alkylamine content with the N/OH molar ratio for the C10- and C18-intercalated compounds are shown in Fig. 7. The actual C18 content of the intercalated compounds well coincided with the theoretical values. In contrast, for the C10-intercalated compounds, approximately 53% of the loaded amounts of C10 was entered into the interlayers regardless of the N/OH molar ratio. As shown in Fig. 8, the basal spacing of C18-intercalated compounds had a tendency to increase at high N/OH molar ratios. The results suggest that the arrangement of alkylamine molecules in the interlayer space changed from monolayer to paraffin type [12] when the alkylamine dose increased. For the C10-intercalated compounds, the interlayers were sufficiently expanded even at low N/OH molar ratios, although all C10 molecules did not enter the interlayer space. A maximum basal spacing was apparently obtained at a N/OH molar ratio of 0.4; this may be due to an irregular arrangement of C10 molecules in the interspaces, which was supported by the broadened XRD peak observed at low diffraction angles. Increasing N/OH molar ratio might improve the regularity of C10 molecules, which decreased the basal spacing. Therefore, the structure of intercalated compounds strongly depends on the length of the alkyl chain and the dose. However, when the molar ratio was higher than 0.6 in both intercalated compounds, no noticeable change in structure was observed, which suggests that the addition of small amounts of alkylamines produces intercalated compounds with sufficiently expanded interlayers.



**Fig. 6.** Effect of the dose of (a) decylamine (C10) and (b) octadecylamine (C18) on the structure of intercalated compounds.



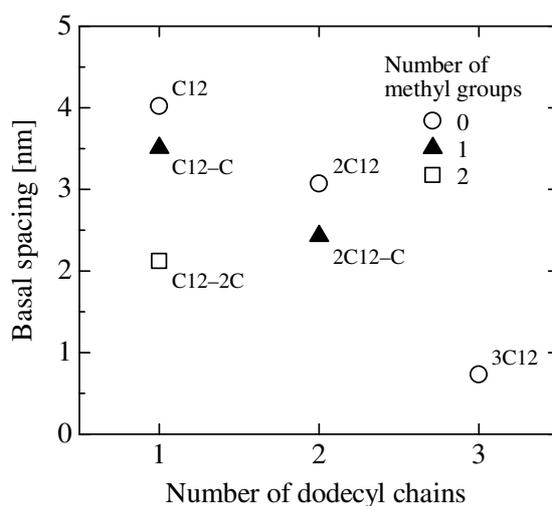
**Fig. 7.** Change in contents of decylamine (C10) and octadecylamine (C18) in the intercalated compounds with the N/OH molar ratio.



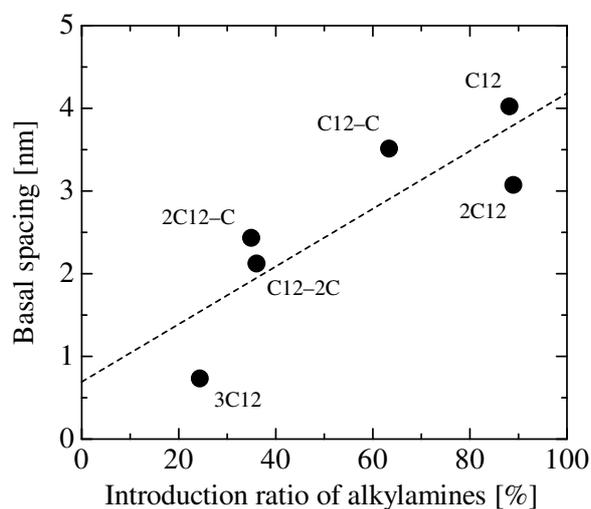
**Fig. 8.** Variation in basal spacing of decylamine (C10)- and octadecylamine (C18)-intercalated compounds with the N/OH molar ratio.

Fig. 9 shows the basal spacing of compounds intercalated with primary, secondary and tertiary amines with different numbers of dodecyl chains and methyl groups. The basal spacing varied depending on the class of dodecylamine, and larger values of basal spacing were observed in the following order: primary > secondary > tertiary. Furthermore, at the same number of dodecyl chains, the basal spacing increased with decreasing number of methyl groups. The results imply that alkylamines with many dodecyl chains and methyl groups may be difficult to bond to the hydroxyl groups in the silicate layers due to steric hindrance, which decreases the interlayer expansion. Fig. 10 shows the variation in the basal spacing with the introduction ratio of the alkylamines, which was defined as a mass ratio of actual content to theoretical value. Larger introduced amounts of alkylamines were also obtained approximately in the order of primary > secondary > tertiary, and the basal spacing tended to increase with

increasing introduced amount. Although the introduced amounts of C12–2C and 2C12–C were almost the same and the steric hindrance of 2C12–C could be larger than that of C12–2C, the basal spacing of the 2C12–C-intercalated compound was slightly larger than that of the C12–2C-intercalated one. Based on the XRD analysis indicating that the diffraction peak attributed to the intercalation of 2C12–C was low and broad (data not shown), this may be because the regularity of 2C12–C in the interspaces was decreased due to the larger number of dodecyl chains.



**Fig. 9.** Basal spacing of compounds intercalated with primary, secondary and tertiary dodecylamines.

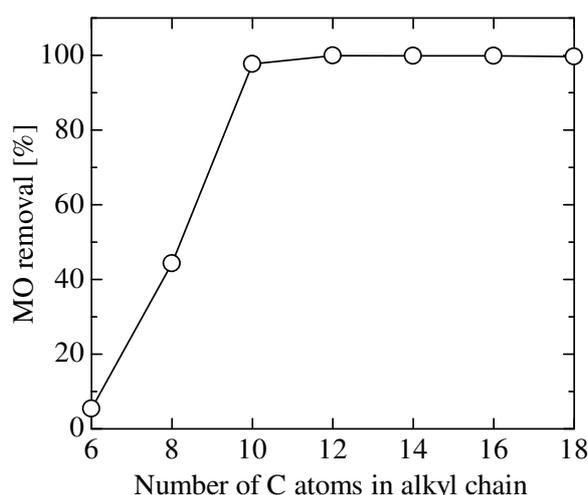


**Fig. 10.** Relationship between basal spacing and introduction ratio of alkylamines.

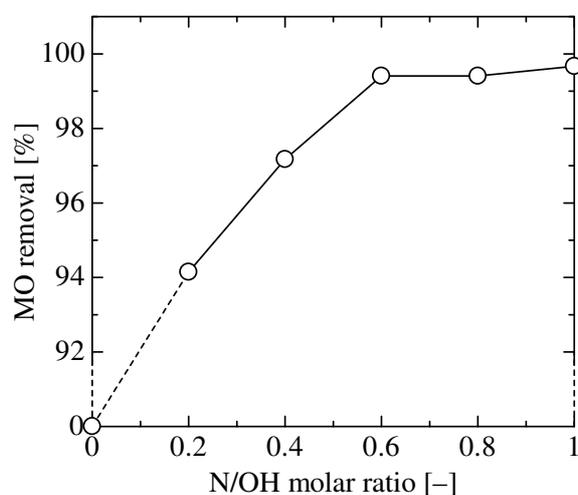
### 3.3. Anionic dye removal properties of intercalated compounds

Fig. 11 shows the MO removal using various primary alkylamine-intercalated compounds as the adsorbents. When using the C10–C18-intercalated compounds, MO rapidly adsorbed on the intercalated compounds; the MO removals higher than 98% were achieved in an adsorption

time of 5 min, which demonstrated the intercalated compounds had high adsorption performance. Although the alkylamine content of C6-intercalated compounds was almost the same as that of the C8-intercalated one (Fig. 3), the latter showed a higher MO removal than the former. The C8-intercalated compound had an ordered structure compared with the C6-intercalated one, suggesting that the adsorption performance is affected by not only the interaction between MO and alkylamine but also the structure of intercalated compounds. Fig. 12 depicts the effects of alkylamine content on the MO removal using the C18-intercalated compounds. Pristine H-octosilicate (i.e., N/OH molar ratio = 0) adsorbed no MO molecules. In contrast, when the N/OH molar ratio was 0.2, the MO removal reached 94% and increased with increasing alkylamine content. The results suggest that even the intercalated compounds with small amounts of alkylamines exhibits good adsorption properties for anionic dyes. The effects of adsorbent dosage and pH dependence on the adsorption and the adsorption kinetics and isotherms must be studied in the future to use the intercalated compounds as the adsorbents in practical applications.



**Fig. 11.** MO removal of primary alkylamine (C6–C18)-intercalated compounds.



**Fig. 12.** Change in MO removal of the C18-intercalated compounds with the N/OH molar ratio.

#### 4. Conclusions

Using primary *n*-alkylamines with different alkyl chain lengths and secondary and tertiary dodecylamines as the guest, H-octosilicate as the host was intercalated in water. The structural changes of the intercalated compounds by the molecular structure and dose of alkylamines were clarified. The results also demonstrated that the intercalation method is effective to obtain the intercalated compounds with well-ordered structures. The primary *n*-alkylamine-intercalated compounds had large interlayer distances compared with the corresponding compounds intercalated with quaternary alkyl ammonium ions and could have the structure that the alkylamine bilayer formed in the interlayer space. In addition, our method using water as the intercalation environment can effectively expand the interlayer distance of intercalated compounds even at relatively low doses of alkylamines, which may contribute to precise control of the structure of intercalated compounds. Using dodecylamines with different numbers of dodecyl chains and methyl groups, the structure of intercalated compounds changed depending on the type of hydrocarbon group and number of hydrogen atoms bonded to the nitrogen atom of the amine. The results can be a guide for preparing the intercalated compounds optimized for designed polymer-clay nanocomposites. The control of the interlayer distance may also lead to the synthesis of rectangular nanosheets via exfoliation. Furthermore, the MO adsorption experiments confirmed the primary *n*-alkylamine (C10–C18)-intercalated compounds showed good properties of MO removal from the aqueous solutions, suggesting that the organosilicates prepared by the intercalation method are promising candidates for treatments of anionic dye-containing waste water by the adsorption.

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