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メタデータ	言語: en 出版者: Elsevier 公開日: 2021-02-16 キーワード (Ja): キーワード (En): Alkylamine, Intercalation, Layered octosilicate, Ordered structure, Solubility 作成者: Iwasaki, Tomohiro メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/10466/00017226">http://hdl.handle.net/10466/00017226</a>

# Effect of solvents on the direct intercalation of decylamine into H-octosilicate

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## Abstract

Decylamine molecules were directly intercalated as guest molecules into a layered silicate, octosilicate, with hydrogen ions in the interlayers (H-octosilicate) as a host material by using a wet process with various solvents of different polarities and decylamine solubilities. The solvent containing H-octosilicate and *n*-decylamine was vigorously stirred at room temperature for 30 min, and the structure of the decylamine-intercalated octosilicate compounds (i.e., organo-octosilicate) was determined via X-ray diffraction (XRD) analysis. The structures of the compounds greatly varied depending on the solvent. The use of a solvent with a relatively high polarity promoted the intercalation of decylamine molecules. In particular, when water, which is a poor solvent for decylamine, was used, the decylamine molecules were well ordered in the interlayer space of H-octosilicate. The interlayer distance corresponded to double the length of the decylamine molecule, suggesting the formation of a decylamine bilayer in the interlayer space. However, the structure became irregular at high temperatures, even in water. In contrast, the use of good solvents for decylamine, such as ethanol and acetone, provided intercalated compounds with disordered structures, suggesting that it was difficult for the decylamine molecules to enter the interlayers. In particular, when nonpolar solvents such as cyclohexane and toluene were used, the intercalation of decylamine hardly occurred. Furthermore, when the intercalation treatment was conducted in aqueous ethanol solutions, the structure depended strongly on the ethanol concentration, and the basal spacing was maximized at an ethanol concentration of 50 vol%. The results of this study suggest that the solvation of decylamine molecules can determine the structure of intercalated octosilicate compounds.

## Keywords

Alkylamine, Intercalation, Layered octosilicate, Ordered structure, Solubility

## 1. Introduction

The intercalation of guest atoms, molecules and ions into organic and inorganic host materials with layered structures, such as graphene (Guo et al., 2018; Paillet et al., 2018) and layered double hydroxide (LDH) (Intasa-Ard et al., 2018; Mishra et al., 2018), is an important treatment for the fabrication of functional materials used for catalysts (Sipos and Pálincó, 2018), electrodes (Nan et al., 2019; Zhao-Karger and Fichtner, 2019), drug carriers (Mallakpour and Hatami, 2019), etc. Among layered materials, layered silicates and clay minerals can often be used to form inorganic nanosheets via exfoliation (Sangian et al., 2018), and they have attracted much attention for use as fillers in nanocomposites. For example, the incorporation of nanosheets in polymeric resins, which have been actively developed around the world, can provide a polymer-based nanocomposite with a high strength and a light weight (Zhu et al., 2019). Octosilicate, which is a layered alkali silicate, has a regular rectangular shape with a relatively smooth surface (Iler, 1964; Iwasaki et al., 2012; Kosuge and Tsunashima, 1995; Sirinakorn et al., 2018). Hence, its nanosheets are promising candidates to use as fillers to create polymer materials with additional functionalities and/or to enhance their properties.

As a pretreatment method for the formation of silicate nanosheets, the intercalation of quaternary ammonium ions with long alkyl chains into the interlayer space is often employed in aqueous solution (Ogawa and Iwata, 2010; Osada et al., 2013). In addition, the intercalation of alkylamines is possible (Kosuge and Tsunashima, 1995; Wang and Pinnavaia, 2003). In this case, various solvents can be used to dissolve alkylamines, and it is empirically known that the solvents may alter the structure of amine-intercalated compounds. However, to the best of our knowledge, the effect of the solvent on the structure of intercalated octosilicate compounds has not been reported.

In this paper, *n*-decylamine ( $C_{10}H_{21}NH_2$ ), which is a primary alkylamine with a long hydrophobic tail, is employed as a model guest molecule for expanding the interlayer space of octosilicate, and several common solvents with different polarities (i.e., decylamine solubilities) are used to study the effects on the intercalation of decylamine and the structure of intercalated compounds.

## 2. Experimental

All reagents, except for the sodium silicate solution used for the synthesis of octosilicate, were purchased from FUJIFILM Wako Pure Chemical (Japan) and used without further purification. Table 1 lists the polarization properties of the solvents used in this work. Deionized

water was used as the water solvent.

Octosilicate with Na<sup>+</sup> ions in the interlayers (denoted as Na-octosilicate) was synthesized via hydrothermal treatment of a sodium silicate solution (Nippon Chemical Industrial; SiO<sub>2</sub>: 23.44 mass%, Na<sub>2</sub>O: 6.29 mass%) at 110°C for 12 days in the absence of seed crystals (Iwasaki et al., 2006). The interlayer Na<sup>+</sup> ions of the obtained Na-octosilicate were ion-exchanged with H<sup>+</sup> ions by soaking Na-octosilicate twice in a 0.1 mol/L hydrochloric acid solution (Kosuge and Tsunashima, 1995). The resulting cation-exchanged 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.

To 20 mL of a solvent listed in Table 1, 0.77 mmol of decylamine (melting point: approx. 12–17°C) was added. The dose of decylamine was determined under the assumption that the chemical formula of H-octosilicate is expressed as Si<sub>4</sub>O<sub>7</sub>(OH)<sub>2</sub> (Borowski et al., 2002) and that the amino groups of decylamine adequately bond to the hydroxyl groups on the surface and in interlayers of H-octosilicate (Kosuge and Tsunashima, 1995). Decylamine has a dielectric constant of 3.31 (Haynes, 2015) and a dipole moment of 1.41 Debye (Narasimha Rao, 1958), indicating relatively low polarity. Therefore, except for water, decylamine was completely dissolved in the organic solvents after carefully stirring the solution at room temperature, and transparent solutions were obtained; water with added decylamine was cloudy. To the solution, 0.1 g of H-octosilicate was added, and the aggregates of H-octosilicate particles were disintegrated in the solvent using an ultrasonic bath (38 kHz, 400 W) for a few minutes. The homogeneous suspension of H-octosilicate obtained was vigorously stirred for 30 min at room temperature to intercalate the decylamine molecules into the interlayer space of H-octosilicate. In addition, when the water solvent was used, intercalation was also performed at 50, 70 and 90°C to study temperature dependence. Furthermore, aqueous ethanol solutions with different ethanol concentrations were used as solvents to vary the solubility of decylamine.

After the intercalation treatment, the suspension was filtered, and the separated precipitate was dried at room temperature for a few days. The structures of the samples were confirmed by a powder X-ray diffractometer (XRD-6100, Shimadzu; CuK $\alpha$ ,  $\lambda$  = 0.154 nm, 30 mA, 30 kV, 1°/min). The thermogravimetry/differential thermogravimetric analysis (TG/DTA) was conducted by a thermogravimetric analyzer (DTG-60, Shimadzu) to investigate the composition and thermal behavior of intercalated compounds.

### 3. Results and discussion

#### 3.1. Effect of solvent polarity

The XRD patterns of decylamine-intercalated compounds prepared in different solvents are shown in Fig. 1 together with the basal spacing  $d$ . All the obtained samples were collected as dry powder, which suggested that the samples contained no large amounts of neat decylamine. Thus, there may be no diffractions from neat decylamine molecules in the XRD patterns and the observed diffractions can attribute to the variation of basal spacing. When cyclohexane and toluene, which are non-polar, and ethyl acetate, which has a relatively low polarity, were used, decylamine molecules were hardly intercalated into the interlayer space of H-octosilicate. In contrast, solvents with a relatively high polarity resulted in the intercalation of decylamine. In addition, the structure of decylamine-intercalated compounds was found to drastically change depending on the solvent used. However, as shown in Fig. 2, no clear correlation between the basal spacing and the representative properties and parameters indicating the degree of polarity shown in Table 1 was observed.

According to the XRD analysis, the compound intercalated in ethanol had a well-ordered structure, but the basal spacing was small, suggesting that it had a structure in which the decylamine molecules lay along the silicate layers, such as a monolayer or bilayer arrangement (Ogawa and Iwata, 2010). The basal spacings of compounds intercalated in either acetonitrile or methanol were quite large because the solvent molecules could be intercalated together with decylamine molecules (e.g., solvent swelling). However, the structures were relatively disordered, broadening the intensity peak at low diffraction angles. Surprisingly, water, which has the highest polarity among the solvents used in this work and hardly dissolves decylamine according to the safety data sheet provided by the supplier, resulted in the formation of an intercalated compound with a fairly well-ordered structure and a relatively large basal spacing. This was possibly because decylamine molecules were not solvated by water molecules (making them unstable in water) but were more stabilized in the interlayer space through the bonds of the amino groups of decylamine to the hydroxide groups of the silicate layer.

In general, the intercalation can be governed by the adsorption/desorption equilibrium between host and guest, which is affected by the concentrations of guest and host in the solution. Actually, the mass ratio of decylamine to H-octosilicate changed the structure of intercalated compounds (Iwasaki, 2020). In contrast, even when the concentration of H-octosilicate in water was increased to 20 mass% as an additional experiment, the similar intercalated compound with a well-ordered structure was obtained. However, when decylamine was directly mixed with dry

H-octosilicate in the absence of solvent, the intercalation was incomplete due to the particle aggregation, resulting in the formation of intercalated compounds with inhomogeneous structures. The results suggest that the water solvent assists the distribution of decylamine molecules and/or the expansion of interlayer spaces.

The TG and DTA curves of the compound intercalated in water are shown in Fig. 3. Although many decylamine molecules desorbed from the compound at temperatures below 200°C, some molecules that relatively strongly bonded to H-octosilicate were thermally decomposed between 350°C and 500°C. Unlike pristine H-octosilicate, the compound intercalated and coated with hydrophobic decylamine possibly has no free water molecules. Using the weight losses of the intercalated compound and H-octosilicate from 30°C to 600°C, the content of decylamine in the compound was estimated as approximately 55 mass%.

As mentioned above, some solvent molecules may be co-intercalated together with decylamine molecules. To investigate the co-intercalation of organic solvent molecules, similar experiments using acetone, acetonitrile, dimethyl sulfoxide, ethanol and methanol as the solvent, in which the intercalation of decylamine was clearly observed (Fig. 1d–1h), were performed in the absence of decylamine. The XRD data of the obtained samples (Fig. 4) confirmed the intercalation of acetonitrile, dimethyl sulfoxide and ethanol molecules whereas acetonitrile and methanol molecules hardly entered into the interlayer space. Simultaneously, the adsorption/grafting of small amounts of solvent molecules on the surfaces of H-octosilicate could also occur. However, the XRD patterns shown in Figs. 1e and 4b suggested that acetonitrile molecules were co-intercalated with decylamine molecules possibly due to a high affinity between them. In contrast, according to the TG/DTA data (Fig. 5) of the samples prepared in the presence and absence of decylamine, a relatively large amount of dimethyl sulfoxide was contained in the decylamine-free sample (Fig. 5c). Therefore, the affinities among decylamine, solvent and H-octosilicate may significantly affect the structure of intercalated compounds.

Although the basal spacing of intercalated compounds prepared in acetone, ethanol and methanol was small (0.92–0.94 nm), these intercalated compounds also showed endothermic reactions at temperatures lower than 200°C and exothermic reactions at approximately 350–500°C (Fig. 5a, 5d and 5e), similar to those with a large basal spacing. The results demonstrate that the structure of intercalated compounds can be controlled by using a suitable solvent with a relatively high polarity.

### 3.2. Intercalation in a water and ethanol solution

It is well known that well-ordered structures can be obtained via ion exchange by exchanging the  $\text{Na}^+$  ions of Na-octosilicate with alkyl quaternary ammonium ions in water (Ogawa and Iwata, 2010). However, the basal spacing (3.32 nm) of our sample obtained in water was almost the same as that (3.3 nm) of the compound obtained through ion exchange with behenyltrimethylammonium ions, which have 22 carbon atoms in the alkyl chain (Ogawa and Iwata, 2010). Considering that the basal spacing of H-octosilicate (0.73 nm) was almost the same as the thickness of a single silicate layer, the distance of the interlayer space containing decylamine molecules was 2.59 nm in our sample. This value was approximately twice the length of a decylamine molecule, which was computed as 1.306 nm using quantum chemical calculation software (Firefly version 8.2.0). Thus, the decylamine bilayer is likely to have formed in the interlayer space. These results also imply that the use of decylamine-soluble solvents can result in intercalated compounds with disordered and unstable structures. In other words, decylamine-insoluble solvents can be effective for obtaining decylamine-intercalated compounds with well-ordered structures.

Subsequently, to vary the water solubility of decylamine, intercalation was performed in water at different temperatures. The XRD patterns of intercalated compounds obtained at higher temperatures are shown in Fig. 6. An increase in temperature could slightly increase the water solubility of decylamine, resulting in a disordered structure. Thus, the solubility of decylamine, i.e., solvation, plays an important role in intercalation, and intercalation at low temperatures can contribute to the stabilization of the arrangement of decylamine molecules in the silicate interlayers.

As mentioned, the use of ethanol and water, a good solvent and poor solvent for decylamine, respectively, provided the intercalated compounds with well-ordered structures; however, the arrangements of decylamine molecules in the interlayer space of these compounds were quite different, possibly due to the different solubility of decylamine. Here, to vary solubility, mixtures of ethanol and water, i.e., aqueous ethanol solutions, with different ethanol concentrations were used, and the effect of solubility on intercalation was examined. The XRD pattern and basal spacing of the intercalated compounds obtained in the ethanol solutions are shown in Figs. 7 and 8, respectively. The structures of the intercalated compounds were greatly affected by the ethanol concentration. For the concentrations between 20 and 50 vol%, the ordered structure was maintained, whereas the structure was disordered for ethanol concentrations of 60 and 70 vol%. At an ethanol concentration of 50 vol%, the basal spacing

was the maximum among the samples, but the intercalated compound could be constructed by multiple structures. The variation in the structure might be due to the change in the reactivity between the amino group of decylamine and the hydroxide group of the silicate layer with the degree of solvation.

#### 4. Conclusion

Decylamine molecules were directly intercalated as guest molecules into the interlayer space of H-octosilicate as a host in various solvents with different polarities. The structures of the decylamine-intercalated compounds depended strongly on the solvent solubility of decylamine, suggesting that the solvation of decylamine can determine the structures of the intercalated compounds. When water, which is a decylamine-insoluble solvent, was used as the solvent, the decylamine molecules were well ordered in the interlayer space and the basal spacing of the intercalated compound was remarkably increased, corresponding to a bilayer of the decylamine molecules. Water has a low impact on the environment and is cost effective. The large basal spacing may contribute to formation of nanosheets via exfoliation. The intercalation of other amines in water must be studied in the future to elucidate the intercalation mechanism.

#### Acknowledgments

This work was supported in part by the Nippon Sheet Glass Foundation for Materials Science and Engineering.

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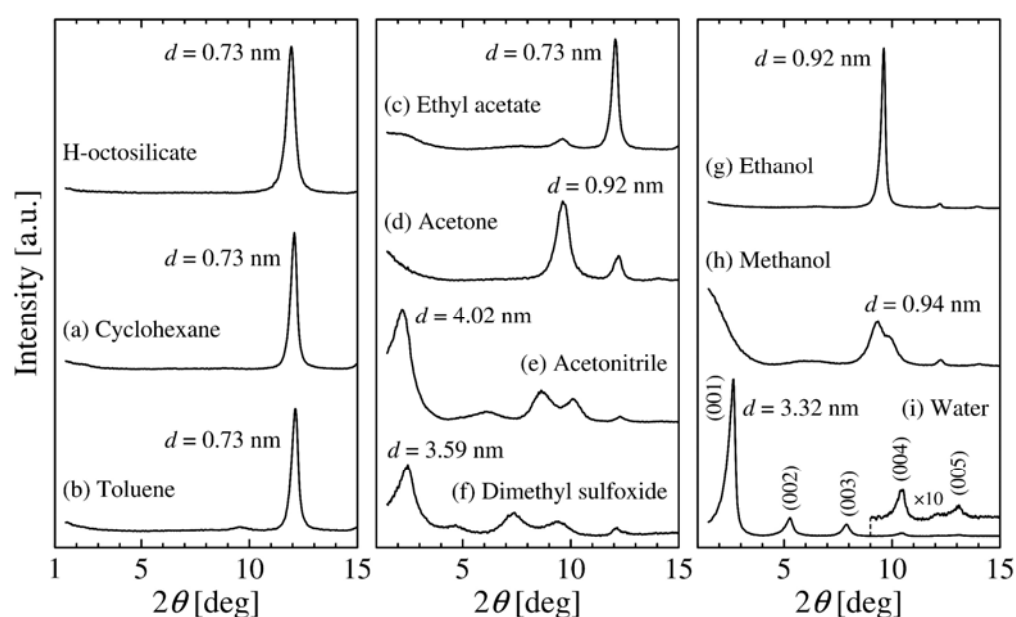
**Table 1** Solvents used in this work.

Solvent	Polarity	Dielectric constant*	Dipole moment* [Debye]	$P'$ <sup>†</sup>	$E_T(30)$ <sup>††</sup> [kcal/mol]
Cyclohexane	Non-polar	2.02	0	−0.2	31.2
Toluene	Non-polar	2.38	0.30	2.4	33.9
Ethyl acetate	Polar (aprotic)	6.02	1.77	4.4	38.1
Acetone	Polar (aprotic)	20.56	2.70	5.1	42.2
Acetonitrile	Polar (aprotic)	35.94	3.90	5.8	46.0
Dimethyl sulfoxide	Polar (aprotic)	46.45	4.05	7.2	45.0
Ethanol	Polar (protic)	24.55	1.74	4.3	51.9
Methanol	Polar (protic)	32.66	1.77	5.1	55.5
Water	Polar (protic)	78.36	1.86	10.2	63.1

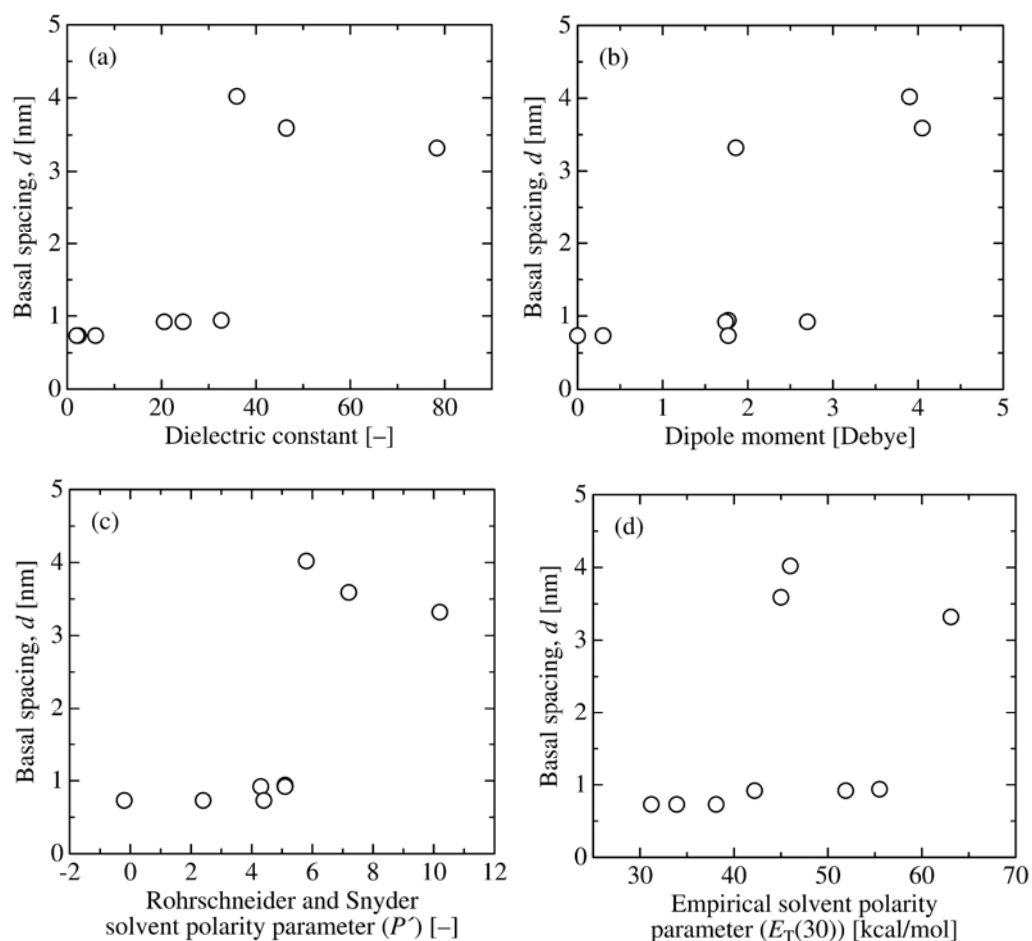
\* Reichardt and Welton (2011)

<sup>†</sup>  $P'$  = Rohrschneider and Snyder solvent polarity parameter, Menet and Thiébaud (1999)

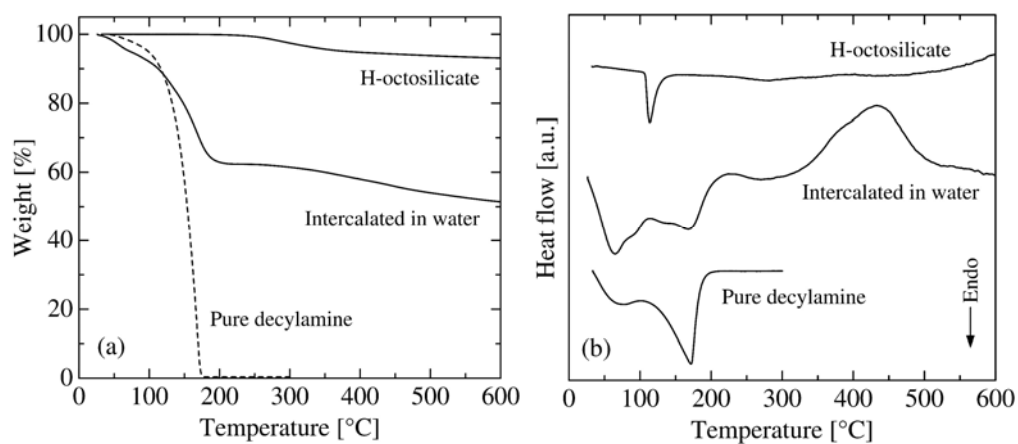
<sup>††</sup>  $E_T(30)$  = empirical solvent polarity parameter, Reichardt and Welton (2011)



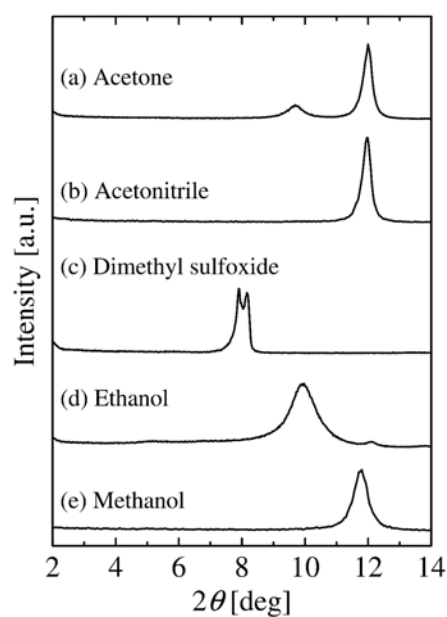
**Fig. 1.** XRD patterns of H-octosilicate and (a–i) decylamine-intercalated compounds prepared in different solvents. The  $d$  values indicate the representative basal spacing.



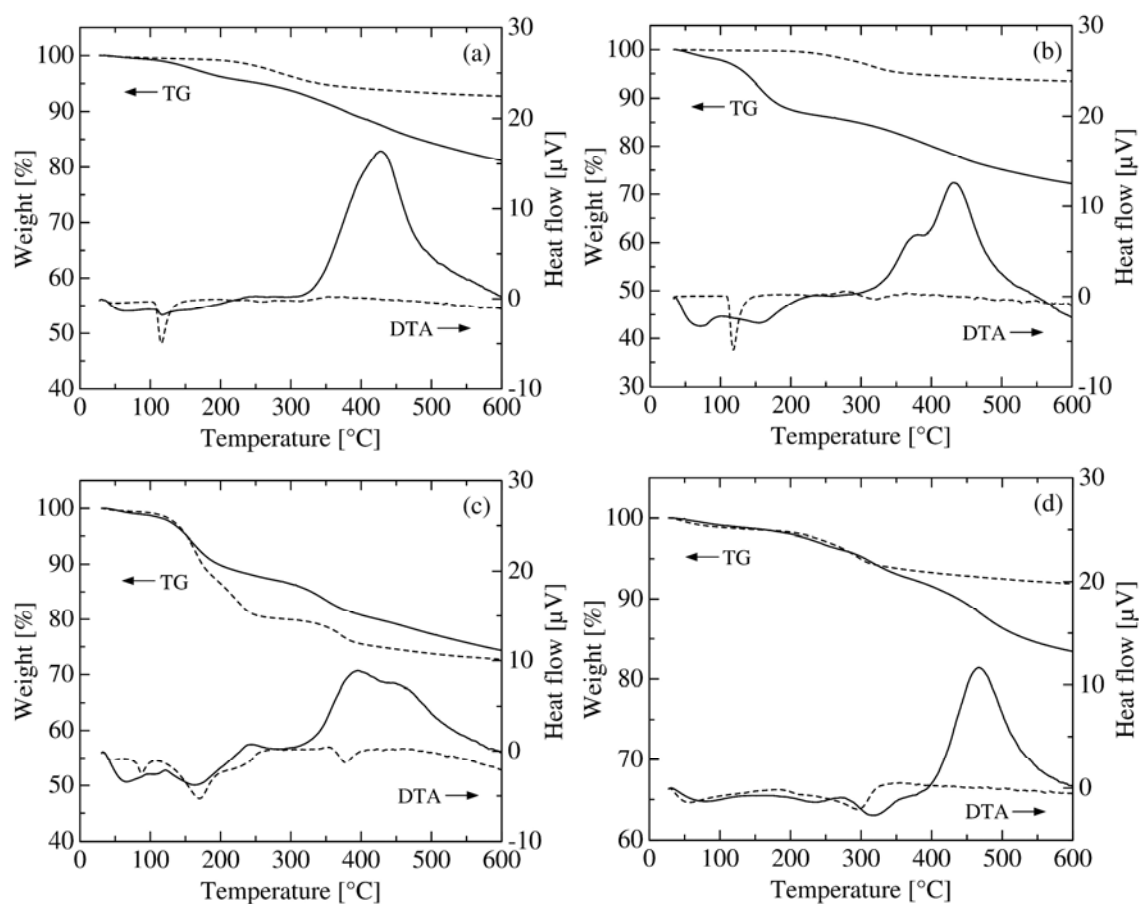
**Fig. 2.** Variations in the basal spacings of samples with the (a) dielectric constant, (b) dipole moment, (c) Rohrschneider and Snyder solvent polarity parameter  $P'$ , and (d) empirical solvent polarity parameter  $E_T(30)$ .

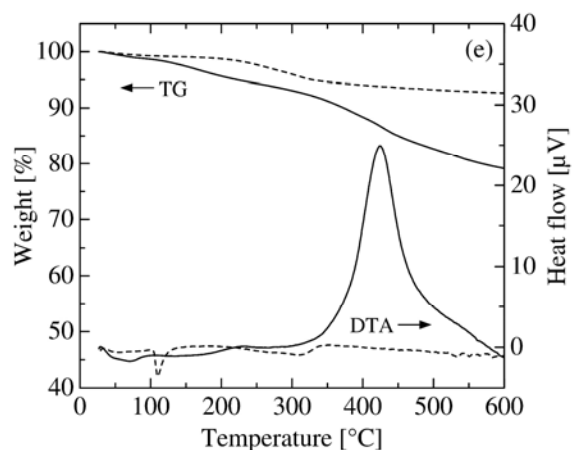


**Fig. 3.** (a) TG and (b) DTA curves of the decylamine-intercalated compound prepared in water.

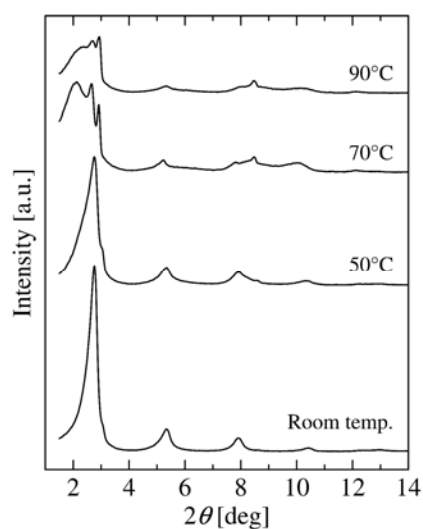


**Fig. 4.** XRD patterns of samples obtained after intercalation treatments using different solvents without decylamine.

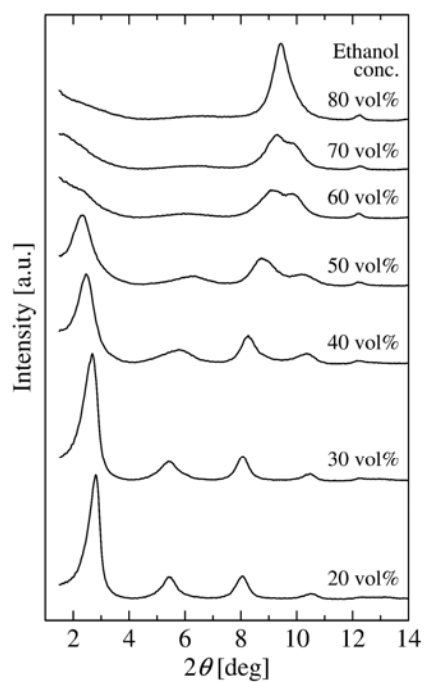




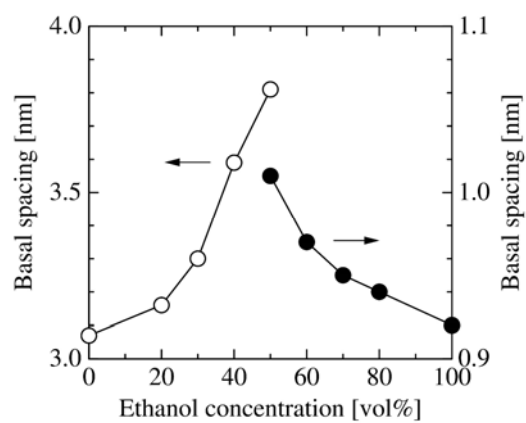
**Fig. 5.** TG/DTA curves of samples obtained after intercalation treatments using different solvents: (a) acetone, (b) acetonitrile, (c) dimethyl sulfoxide, (d) ethanol and (e) methanol. The solid and broken lines for each solvent correspond the samples treated in the presence and absence of decylamine, respectively.



**Fig. 6.** Effect of temperature on the structure of compounds intercalated in water.



**Fig. 7.** XRD patterns of samples prepared in aqueous ethanol solutions with different ethanol concentrations.



**Fig. 8.** Change in basal spacing with ethanol concentration.