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Adsorption of Alcohols from Aqueous Solutions into a Layered Silicate Modified with Octyltrichlorosilane

Ikuko Fujita,[†] Kazuyuki Kuroda,[†,‡] and Makoto Ogawa*[,§]

Department of Applied Chemistry, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo 169-8555, Japan,
Kagami Memorial Laboratory for Materials Science and Technology, Waseda University,
Nishiwaseda 2-8-26, Shinjuku-ku, Tokyo 169-0051, Japan, and Department of Earth Sciences,
Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan

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The adsorption of 1-hexanol and 1-butanol from water on the organically modified layered silicates, derived from magadiite by silylation with octyltrichlorosilane, was investigated. The degree of the interlamellar surface coverage of magadiite with octylsilyl groups affected the adsorptive properties. The modified magadiites with lower coverage adsorbed alcohols from aqueous solutions with lower concentrations. Both 1-hexanol and 1-butanol were adsorbed from aqueous solutions with very similar relative concentrations, suggesting that the solubilities of 1-hexanol and 1-butanol in water were correlated with the adsorption behavior. 1-Hexanol was adsorbed preferentially from a 1-hexanol/1-butanol aqueous mixture under limited conditions.

Introduction

Organic modification of layered solids is a way to construct inorganic−organic hybrids with specific functions such as adsorptive and swelling properties.[1,2] Among possible functions, adsorptive properties of organically modified layered solids have been investigated extensively.[1−15] The interlayer surface modification of layered silicates may lead to adsorbents with specific molecular sieving ability as well as novel functional materials by further accommodation of functional units into those organically modified materials. For such purposes, cation exchange of interlayer cations of layered solids with organoammonium ions has been investigated so far.[3−11] Adsorption of aromatic hydrocarbons[3−7] and *n*-alkyl alcohols[8−11] into organoammonium clays from aqueous solutions was reported. The size and the nature of organoammonium ions significantly affect the properties of the resulting hybrid materials.

Immobilization of organic groups through a covalent bond is an alternative way to modify the interlamellar surface properties of layered solids. The reactions between organosilanes and hydroxylated surfaces lead to a creation of organically modified surfaces where organic moieties are covalently attached. Silylation of the interlayer silanol groups of layered silicates has been conducted to prepare inorganic−organic nanocomposites.[15−21] Organosilanes containing various organic groups, such as alkyl,[15−18] perfluoroalkyl,[19] phenyl,[20] and vinyl[21] groups, have been used for the surface modification of layered silicates. The silylation has recently been applied to the immobilization of organosilyl groups into layered titanates.[22]

We have reported the adsorption of alcohols into magadiite, a layered silicate with the nominal composition of $Na_2H_2Si_{14}O_{30}\cdot nH_2O$,[23] modified with octylsilyl groups.[15,24] The surface properties were designed to bind guest species by controlling the degree of silylation as well as the use of organochlorosilanes with different functionality which give new silanol groups in the interlayer space after the surface modifications.[15,24] The inorganic−organic hybrid hosts bind *n*-alkyl alcohols in their expandable interlayer spaces with

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[*] To whom correspondence should be addressed. Fax: 81-3-3207-4950. E-mail: makoto@waseda.jp.
[†] Department of Applied Chemistry.
[‡] Kagami Memorial Laboratory for Materials Science and Technology.
[§] Department of Earth Sciences.

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the cooperative effects of the organophilic octyl groups and possible hydrogen bonding. Interestingly, the octylsilylated magadiites adsorb *n*-alkyl alcohols quantitatively to give composites with layered hybrids with the controlled gallery heights. Thus, further study on the preparation and adsorptive properties of organically modified silicates is worth investigating from the viewpoints of novel adsorbent design as well as advanced materials applications. Here we report the adsorption of alcohols, 1-butanol and 1-hexanol, from aqueous solutions into the octylsilylated magadiites. Three differently modified magadiites were examined as adsorbents to search the effects of the interlamellar surface coverage with organic groups on the adsorptive properties.

Experimental Section

Materials. High-purity sodium silicate (SiO_2: 21.1 mass % and Na_2O: 6.57 mass %, Nihon Chemical Ind. Co.), SiO_2 (special grade, Wako Chemicals Co.), HCl (special grade, Junsei Chemical Co.) and NaOH (special grade, Junsei Chemical Co.) were used for the preparation of Na-magadiite. DTMA chloride (special grade, Tokyo Kasei Ind. Co.) and octyltrichlorosilane (abbreviated as C_8SiCl_3, Tokyo Kasei Co., extra pure grade) were used as received. Distilled dry toluene (special grade, Kanto Chemical Co., distilled over sodium) was used as a solvent for silylation. Acetone (special grade, Kokusan Chemical Co.) and pure water were used for washing the silylated derivatives. *n*-Decane (Kanto Chemical Co.), 1-butanol (abbreviated C4OH, Kokusan Chemical Co., special grade), and 1-hexanol (abbreviated C6OH, Junsei Chemical Co., special grade) were special grade chemicals and used without further purification.

Na-magadiite and DTMA-magadiite. Na-magadiite was prepared by a method reported previously.[18] High-purity sodium silicate, SiO_2, and distilled water were mixed at the ratio of $SiO_2/NaOH/H_2O = 1:0.23:18.5$. The mixture was sealed in a Teflon-lined autoclave (Taiatsu Glass Co., TAF-SR-100) and treated hydrothermally at 150 °C for 2 d. The product was washed with a dilute aqueous solution of NaOH (pH = 9.0−9.5) and dried at 40 °C for 2 d. Na-magadiite was characterized by XRD and ^{29}Si CP/MAS NMR. The basal spacing was 1.55 nm, and the diffraction pattern coincided with the reported one.[22] The ^{29}Si MAS NMR spectrum showed the signals characteristic to Q^3 and Q^4 environments of Si atoms of magadiite. From these observations, the formation of Na-magadiite was confirmed.

Dodecyltrimethylammonium-magadiite (abbreviated as DTMA-magadiite) was prepared by the ion exchange of Na-magadiite with DTMA chloride and was used as the intermediate for silylation.[17] The basal spacing of the DTMA-magadiite was 2.8 nm, indicating the successful ion exchange of Na^+ with $DTMA^+$. On the basis of the CHN analysis and TG of the product (C: 2.45 mass %, H: 4.67 mass %, N: 1.71 mass %, and SiO_2: 63.0 mass %), the amount of DTMA was estimated to be 1.49 mol DTMA/14SiO_2.

Silylation. Silylation was conducted by a method reported previously.[15] DTMA-magadiite was dried under a reduced pressure at 100 °C for 2 h and was mixed with toluene and a fixed amount of octyltrichlorosilane. Three silylated magadiites with different degrees of coverage were synthesized by changing the amount of the silylating reagent added. The reaction mixture was refluxed under an N_2 flow at 110 °C for 2 d. The centrifuged precipitates were washed with toluene twice, a mixed solution of HCl (0.1 mol L^{-1}) and acetone (1:1 in volume) three times, H_2O and acetone (1:1 in volume) until Cl^- free, and acetone twice. The products were dried at 40 °C for 2 d to yield the silylated derivatives.

Adsorption of Alcohols into Silylated Magadiites. Alcohols used for the adsorption measurements were 1-butanol and 1-hexanol. The silylated magadiite (0.05 g) was mixed with 20 mL of an aqueous solution of alcohol (1-hexanol, $0-3 \times 10^{-2}$ mol L^{-1}, 1-butanol, $0-5 \times 10^{-1}$ mol L^{-1}) in a centrifuge tube at room temperature for 2 d with magnetic stirring. The adsorbents were separated by centrifugation (at 3500 rpm for 10 min), and the alcohol concentration of the supernatant was determined by gas chromatography to determine the amounts of adsorbed alcohols. The adsorbed amounts were calibrated by a blank test. Alcohol concentrations were calculated from the measured GC peak areas using a series of external standards. The adsorbents were analyzed by XRD. The adsorption of alcohols from *n*-decane (40 mL) was also examined.

Table 1. Chemical Composition and the d-Spacing of the Silylated Magadiites

amounts of silylating reagent (per 14SiO_2)	C (mass %)	H (mass %)	SiO_2 (mass %)	amounts of silyl groups (per 14SiO_2)	d-spacing (nm)	surface coverage (%)
0.80	9.81	1.84	89.3	0.96	1.84	0.55
1.1	10.7	2.34	80.5	1.16	1.99	0.45
2.0	15.7	2.58	82.7	1.67	2.14	0.32

Characterization. X-ray powder diffraction patterns were obtained by a Mac Science MXP[3] diffractometer (monochromatic Cu Kα) for the characterization of the products and a Mac Science M03XHF[22] diffractometer (Mn-filtered Fe Kα) for the measurement of low diffraction angles. IR spectra were recorded on a Perkin-Elmer Fourier transform Spectrum One spectrometer using a KBr disk technique. TG curves were measured by a Mac Science 2000S instrument with a heating rate of 10 °C/min under a dry air flow. CHN analysis was conducted with a Perkin-Elmer PE2400II instrument. Solid-state ^{29}Si CP/MAS NMR spectra were recorded on a JEOL JNM-CMX400 spectrometer at a resonance frequency of 79.42 MHz with a 90° pulse and a recycle delay of 5 s. The spinning speed of samples was 6 kHz. Tetramethylsilane (TMS) was used as a reference for the measurement. H_2O adsorption measurements were carried out at 25 °C using a BELSORP18 apparatus. Prior to the measurement, samples were outgassed at 80 °C for 6 h under vacuum (10^{-1} Torr). Gas chromatograms were recorded on a Hewlett-Packard 5890 SERIES II with a flame ionization detector, and a capillary column (HP-innowax; inner diameter 0.25 mm, phase thickness 0.25 μm, length 30 m, poly(ethylene glycol)-coated) was used with N_2 as the carrier gas.

Results and Discussion

Preparation of Adsorbents. The silylation of magadiite was confirmed by the X-ray diffraction patterns, chemical analyses, IR and NMR spectra, and thermal analyses of the products as reported previously.[15,24] The chemical compositions of the products are shown in Table 1. Three silylated magadiites with different interlamellar surface coverages of octylsilyl groups were obtained, and hereafter the products were designated as C8Si(0.96)-, C8Si(1.16)-, and C8Si(1.67)-magadiites, where the number in parentheses indicates the molar ratio of the attached octylsilyl group to the 14SiO_2 unit of magadiite.

Figure 1 shows the water adsorption/desorption isotherms on C8Si(1.16)- and C8Si(1.67)-magadiites. The adsorption capability varied significantly, depending on the coverage with octylsilyl groups; C8Si(1.16)-magadiite adsorbs larger amounts of water molecules than C8Si(1.67)-magadiite does. It is explained by the difference in the population of the interlayer silanol groups interacting with water molecules. The water adsorption abilities affect the adsorption of alcohols from water.

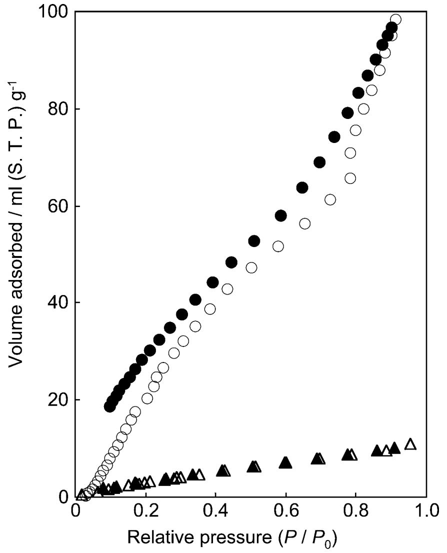

Figure 1. Water adsorption/desorption isotherms of ○/●: C8Si(1.16)-magadiite, and △/▲: C8Si(1.67)-magadiite.

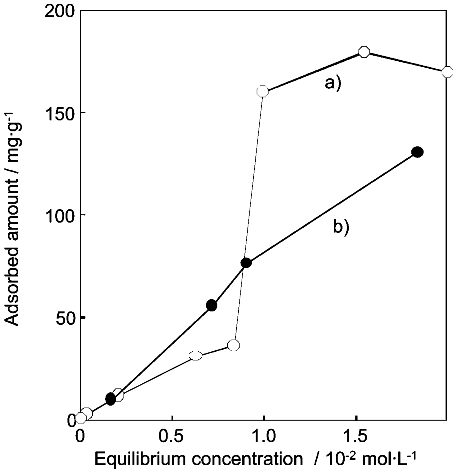

Figure 2. Amount of adsorbed C6OH for C8Si(0.96)-magadiite as a function of equilibrium concentration ○: from aqueous solution and ●: from *n*-decane.

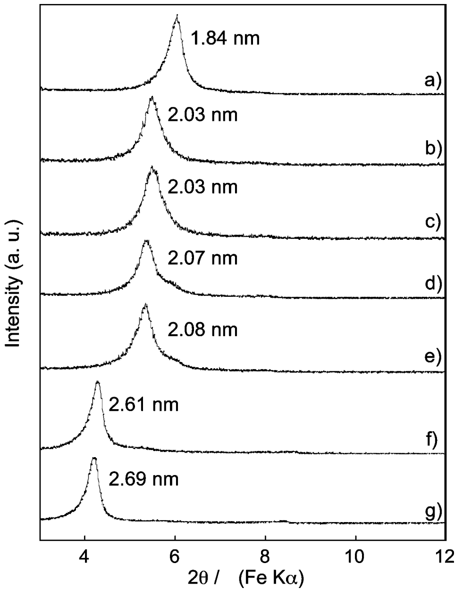

Figure 3. XRD patterns of (a) C8Si(0.96)-magadiite and the silylated derivative dispersed in C6OH aqueous solutions at the alcohol concentrations of (b) 0 mol L^{-1} (in water), (c) 2.39 mmol L^{-1}, (d) 7.17 mmol L^{-1}, (e) 9.43 mmol L^{-1}, (f) 20.1 mmol L^{-1}, and (g) 24.2 mmol L^{-1}.

Adsorption of 1-Hexanol to Silylated Magadiites. The adsorption isotherms of 1-hexanol into C8Si(0.96)-magadiite from *n*-decane and water are shown in Figure 2. According to the Giles and Smith classification,[25] the adsorption isotherm from *n*-decane follows the type C. The C-type isotherm is linear and suggests partitioning. The amounts of adsorbed 1-hexanol increased linearly with the increase in the concentration up to 2.0×10^{-2} mol L^{-1} and reached the maximum of ~1.3 mol/14SiO$_2$, which corresponds to 122 mg/g.

On the other hand, the adsorption of 1-hexanol on C8Si-(0.96)-magadiite from water yielded an S-type isotherm. When the equilibrium concentration was low, only a small amount of 1-hexanol was adsorbed. With the increase in the equilibrium concentration, the amount of adsorbed 1-hexanol increased. There is a step in the adsorption isotherm at the equilibrium concentration of $\sim 1.0 \times 10^{-2}$ mol L^{-1}. The amounts of adsorbed 1-hexanol dramatically increased at this concentration. No further adsorption occurred even when the concentration was increased further, and the maximum adsorption amount was ca. 1.5 mol/14SiO$_2$, which corresponds to 122 mg/g. S-type adsorption occurs when the following conditions are fulfilled: the solute molecule (a) is monofunctional, (b) has moderate intermolecular attraction, and (c) meets strong competition from solvent or another adsorbed species.[25] 1-Hexanol meets these requirements so that the S-type adsorption isotherm is plausible.

In our separate paper on the reaction of the silylated magadiites with neat 1-alkanols, we have reported that the basal spacing of the silylated magadiites increased upon the adsorption of alcohols to accommodate them in the interlamellar space.[24] The increased basal spacing of organoammonium-vermiculites by the adsorption of 1-pentanol and 1-butanol was also reported previously.[10,11] The 1-hexanol adsorbed from water was also thought to occupy the interlayer region, since the maximum adsorbed amounts are large. The changes in the X-ray diffraction patterns of C8Si-(0.96)-magadiite by the reaction with aqueous and *n*-decane solutions of 1-hexanol are shown in Figures 3 and 4, respectively. When C8Si(0.96)-magadiite was treated with an aqueous solution of 1-hexanol with low concentrations ($< \sim 10$ mmol L^{-1}), the basal spacing increased slightly to 2.03−2.08 nm. Since the amounts of adsorbed 1-hexanol are very small at the concentration range (Figure 2), it was thought that the slight increase in the basal spacing was caused by the adsorption of water molecules. The hydration of C8Si(0.96)-magadiite led to the basal spacing of 2.03 nm, supporting the above-mentioned discussion. In addition to the presence of water molecules, the possibility of the desorption of alcohol during the measurements cannot be excluded completely. Accordingly, a detailed discussion on the small difference in the basal spacing is difficult at present.

When the adsorption was conducted from the concentrated aqueous solutions ($> \sim 10$ mmol L^{-1}), the basal spacing of C8Si(0.96)-magadiite increased to 2.5−2.6 nm. The large amounts of adsorbed 1-hexanol were thought to occupy the interlayer space to cause the expansion.

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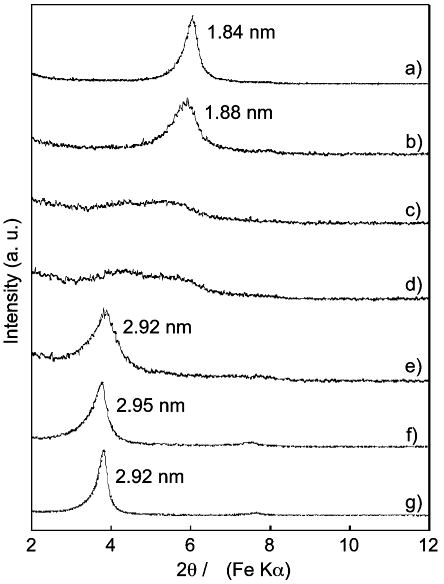

Figure 4. XRD patterns of (a) C8Si(0.96)-magadiite and the silylated derivative dispersed in C6OH/decane mixtures at the alcohol concentrations of (b) 2.09 mmol L^{-1}, (c) 8.37 mmol L^{-1}, (d) 10.4 mmol L^{-1}, (e) 21.0 mmol L^{-1}, (f) 210 molm L^{-1}, and (g) dispersed in C6OH.

On the other hand, the basal spacing of C8Si(0.96)-magadiite did not change upon the adsorption of 1-hexanol from a diluted *n*-decane solution (2.09 mmol L^{-1}) (Figure 4b). Note that decane did not intercalate into the interlayer space of the silylated magadiites as reported previously.[24] When the concentrated solution was employed, the basal spacing increased to ~2.9 nm. The two diffraction peaks coexist when the adsorption was conducted from the solutions in the concentration range of 8.37−10.4 mmol L^{-1}. The increased basal spacing of 2.92 nm was same as that (2.92 nm) of C8Si(0.96)-magadiite treated with neat 1-hexanol. From these observations, the adsorbed 1-hexanol formed densely packed aggregates in the interlayer space with octylsilyl groups, as reported for the products obtained by the reaction of modified magadiites with neat *n*-alkyl alcohols.[24]

We have already discussed the possible arrangements of 1-alkanols in the interlayer space of the silylated-magadiites from the variation of the basal spacings and proposed that the bilayer arrangements of 1-alkanols and octylsilyl groups were plausible.[24] When the adsorption of 1-hexanol from *n*-decane was saturated, the intercalated 1-hexanol forms a bilayer aggregate in the gallery space, as reported previously for the products obtained by the reaction with neat alcohols.[24] On the other hand, the basal spacing was smaller when the adsorption was conducted from aqueous solutions. The adsorbed 1-hexanol is thought to occupy the interlayer space to increase the basal spacing (~2.5 nm); however, the microstructure of the C8Si(0.96)-magadiite containing 1-hexanol is difficult to discuss due to the possible coexistence of adsorbed water molecules.

Effects of the Interlamellar Surface Coverage on the Adsorption of Alcohols. C8Si(1.67)-magadiite also adsorbed 1-hexanol from aqueous solution. Figure 5 shows the variation of the basal spacings of C8Si(0.96)-magadiite, C8Si(1.16)-magadiite, and C8Si(1.67)-magadiite after the adsorption of 1-hexanol as a function of the concentration.

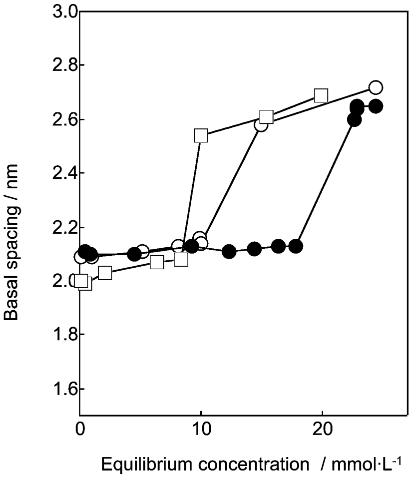

Figure 5. Basal spacing of silylated derivatives after adsorption of C6OH from aqueous solutions as a function of the equilibrium concentration of C6OH. □: C8Si(0.96)-magadiite, ○: C8Si(1.16)-magadiite, and ●: C8Si-(1.67)-magadiite.

When the coverage of octylsilyl groups is low, the increase in the basal spacing occurred from lower concentrations (C8Si(0.96)- < C8Si(1.16)- < C8Si(1.67)-magadiites). C8Si-(1.67)-magadiite adsorbed 1-hexanol to give the basal spacing of ~2.6 nm only when 1-hexanol was adsorbed from concentrated solutions (> 20 mmol L^{-1}). The difference was explained by the different affinity of the silylated magadiites to 1-hexanol. The interactions between OH groups of alcohols and silanol groups in modified magadiites are one possible driving force for the adsorption of 1-hexanol.[15] The concentrations of hydrophobic octylsilyl groups and hydrophilic silanol groups in the interlayer spaces were different, depending on the coverage of octylsilyl groups. This difference was thought to cause the difference in the affinity to 1-hexanol.

Difference between the Adsorption of 1-Butanol and 1-Hexanol. 1-Butanol was also adsorbed into C8Si(1.16)-magadiite and C8Si(1.67)-magadiite from water, and the variations of the basal spacings after the adsorption of 1-butanol are shown in Figures 6 and 7, respectively. Similar to the adsorption of 1-hexanol, the basal spacing of C8Si-(1.16)-magadiite slightly increased to ~2 nm after the adsorption of 1-butanol from the aqueous solutions with low concentrations (<15.2 mmol L^{-1}). The basal spacing increased to ~2.5 nm when 1-butanol was adsorbed from the solutions with high concentrations (>200 mmol L^{-1}). The maximum of the basal spacing is smaller than that (Figure 6(i); 2.77 nm) of C8Si(1.16)-magadiite treated with neat 1-butanol. This tendency is observed for the adsorption of 1-hexanol. The basal spacing of C8Si(1.67)-magadiite also increased to ~2.5 nm after the adsorption of 1-butanol from the solutions with high concentrations (>25 mmol L^{-1}). The basal spacing is smaller than the value observed when the adsorption was conducted from neat 1-butanol. The basal spacings of the C8Si(1.16)- and C8Si(1.67)-magadiites are very similar when the adsorption of 1-butanol was saturated.

Figure 8 represents the change in the basal spacing of C8Si(1.16)-magadiite and C8Si(1.67)-magadiite as a function of the concentration of 1-butanol. As observed for the adsorption of 1-hexanol from aqueous solutions (Figure 5),

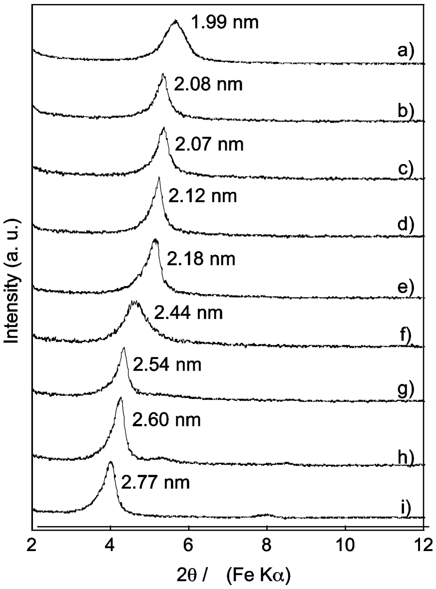

Figure 6. XRD patterns of (a) C8Si(1.16)-magadiite and the silylated derivative dispersed in C4OH aqueous solutions at the alcohol concentrations of (b) 0 mmol L^{-1} (in water), (c) 0.876 mmol L^{-1}, (d) 95.0 mmol L^{-1}, (e) 149 mmol L^{-1}, (f) 199 mmol L^{-1}, (g) 381 mmol L^{-1}, (h) 508 mmol L^{-1}, and (i) dispersed in C4OH.

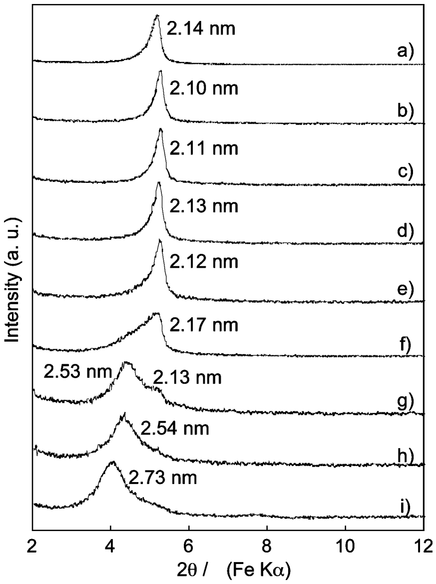

Figure 7. XRD patterns of (a) C8Si(1.67)-magadiite and the silylated derivative dispersed in C4OH aqueous solution at the alcohol concentrations of (b) 0 mmol L^{-1} (in water), (c) 93 mmol L^{-1}, (d) 149 mmol L^{-1}, (e) 199 mmol L^{-1}, (f) 2.44 mmol L^{-1}, (g) 381 mmol L^{-1}, (h) 508 mmol L^{-1}, and (i) dispersed in C4OH.

1-butanol was adsorbed into C8Si(1.16)-magadiite from lower concentration if compared with that into C8Si(1.67)-magadiite.

As shown in Figures 5 and 8, the adsorption of 1-hexanol and 1-butanol into C8Si(1.16)-magadiite occurred from different concentrations (10 and 400 mmol L^{-1} for 1-hexanol and 1-butanol, respectively). To evaluate the differences by solutes in the uptake from water, the basal spacings are correlated with relative concentration (C_e/C_s; where C_e and C_s are the equilibrium concentration and water solubility, respectively) as shown in Figure 9. The adsorption of 1-hexanol and 1-butanol occurred from very similar C_e/C_s values, suggesting that the solubilities of 1-hexanol and 1-butanol in water probably affect the adsorption behavior.

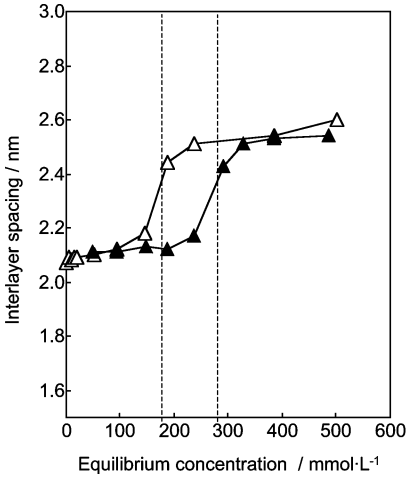

Figure 8. Interlayer spacing of silylated derivatives after adsorption of C4OH as a function of the equilibrium concentration of C4OH. ●: C8Si-(1.16)-magadiite. and ○: C8Si(1.67)-magadiite.

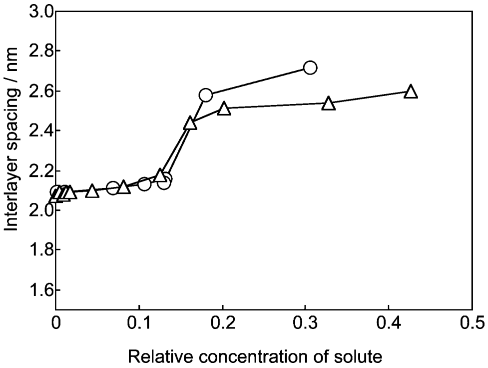

Figure 9. Interlayer spacing of C8Si(1.16)-magadiite after adsorption of alcohols from water as a function of the relative concentration of the solute, ○: C6OH and △: C4OH.

Table 2. Amount of Alcohols Adsorbed into C8Si(1.16)-magadiite from C6OH/ C4OH/Water Mixtures

	C6OH		C4OH	
C4OH/ C6OH	concentration (mmol L^{-1})	adsorbed amount (mg g^{-1})	concentration (mmol L^{-1})	adsorbed amount (mg g^{-1})
1	22.3	160	21.5	8.3
2	19.7	240	41.3	140

The concentration-dependent adsorption mentioned above suggests the possible separation from mixed solutions by means of adsorption into the modified magadiites. When the adsorption into C8Si(1.16)-magadiite was conducted from aqueous solutions containing 1-butanol (22.3 mmol L^{-1}) and 1-hexanol (21.5 mmol L^{-1}), 1-hexanol was adsorbed on C8Si(1.16)-magadiite preferentially, as shown in Table 2. The ratio of partitioning coefficient (K_d for C6OH/Kd for C4OH) was derived for the present experimental condition to be 16, obviating the preferential adsorption of C6OH.

In the adsorption of alcohols from aqueous environments, the concentrations of alcohols in the environments, where the amounts of adsorbed alcohols are steeply increased, depend on the kind of alcohols. The amounts of adsorbed 1-hexanol increased steeply at lower concentration than 1-butanol. When the two kinds of alcohols are adsorbed at the same time and when the concentrations of both alcohols are between 180 and 280 mmol L^{-1}, 1-hexanol was preferentially adsorbed. Under the coexisiting conditions, the concentrations of the steep increase of the adsorption should be different from those of the single components (probably shifted to lower concentrations). Notwithstanding this deviation, the above statement can be applicable to the present system in a qualitative manner. Further systematic studies of the adsorption of various kinds of alcohols onto silylated-magadiites with different alkyl groups and surface coverage are required to clarify the mechanism of the preferential adsorption.

Conclusions

The interlamellar space of magadiite was organically modified with octyltrichlorosilane, and the degree of the interlayer surface coverage was varied. The modified magadiites adsorbed 1-hexanol and 1-butanol from aqueous solutions. The interlayer surface coverage of octylsilyl groups affected the adsorption behavior. The octylsilylated magadiite with lower surface coverage adsorbed alcohols from low concentrations, while that with higher surface coverage adsorbed alcohols from higher concentrations. When the octylsilylated magadiites with lower coverage were used, 1-hexanol was adsorbed from relatively low-concentration solutions if compared with 1-butanol and the preferential adsorption of 1-hexanol from a 1-hexanol/1-butanol mixture was observed under limited conditions.

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