

PREPARATION OF KAOLINITE-AMINO ACID INTERCALATES DERIVED FROM HYDRATED KAOLINITE

MAKOTO SATO

Department of Metallurgical and Inorganic Materials, Nagoya Municipal Industrial Research Institute, 3-4-41, Rokuban, Atsuta-ku, Nagoya, 456 Japan

Abstract—Intercalation of amino acids into 10.0-Å hydrated kaolinite was studied by powder X-ray diffraction (XRD), differential thermal analysis-thermal gravimetry (DTA-TG), and infrared (IR) spectroscopy. Intercalation was found to be dependent on the chain-length, pH, and the concentration of the amino acid zwitterion. Near the isoelectric point, fully intercalated phases were obtained in solutions of concentration >0.5–1 M for glycine (Gly), 2–3 M for β -alanine (β -Ala), and 12 M for both γ -aminobutyric acid (γ -Aba) and δ -aminovaleric acid (δ -Ava). ϵ -aminocaproic acid (ϵ -Aca) with a long chain ($C = 6$) was only partially intercalated. Intercalated amino acid formed a mono-molecular arrangement with the alkyl chain tilting toward the layer at an angle related to H_2O content. The compositions of the intercalates of the Gly and β -Ala are $Al_2Si_2O_5(OH)_4(Gly)_{0.67} \cdot 0.24H_2O$ and $Al_2Si_2O_5(OH)_4(\beta-Ala)_{0.63} \cdot 0.25H_2O$, respectively, based on TG data. From IR data, Gly and β -Ala molecules are found intercalated as zwitterions and these molecules form hydrogen bonds with both the Al-OH and Si-O surfaces of kaolinite. Washing the intercalate with water produced a hydrated kaolinite, which may form a second amino-acid intercalate of high order. Thus, hydrated kaolinite intercalates or deintercalates amino acids depending on concentration and conditions.

Key Words—Amino Acid, CMS Source Clay KGa-1, Differential Thermal Analysis, Hydrated Kaolinite, Intercalation, Infrared Spectroscopy, Kaolinite, Thermogravimetric Analysis, Powder X-ray Diffraction.

INTRODUCTION

The interaction between clay minerals and amino acids has attracted considerable attention relating to the role of clay minerals in metabolism of organic substances in the environment and in peptide formation in the prebiotic era (Theng, 1974). Many studies on kaolin minerals have focused on phenomena occurring on external surfaces of particles, such as selective adsorption, catalysis, and polymerization (*e.g.*, Lahav and Chang, 1976). In contrast, only a few studies involve the intercalation of amino acids in kaolin minerals. Carr and Chih (1971) reported the direct intercalation of several amino acids in hydrated halloysite. Weiss *et al.* (1963) prepared intercalates of kaolinite with potassium salts of glycine, alanine, and lysine using hydrazine as an entraining agent. In both studies, however, the details of intercalation were not reported.

A synthetic analog of hydrated halloysite was first prepared by Wada (1965). He obtained an 8.4-Å hydrated nacrite by water-washing of a potassium-acetate intercalate. Later, Costanzo and coworkers (Costanzo and Giese, 1985; Costanzo *et al.*, 1980, 1984a) reported a method where kaolinite (Kao)-dimethylsulfoxide (DMSO) intercalate was treated with fluoride to displace hydroxyls at the edges and on the interlayer surfaces of kaolinite, and then washed with water. They obtained four hydrates: an 8.4-Å hydrate, an 8.6-Å hydrate, and two 10-Å hydrates. The 8.4-Å hydrate was shown to be useful as an intermediate for intercalation of various organic molecules (Costanzo and Giese, 1990). On the other hand, Raythatha and Lip-

sicas (1985) presented a method where a 10.0-Å and an 8.6-Å hydrated kaolinite could be obtained by washing the Kao-DMSO intercalate with methanol and water and without fluoride treatment.

The method of Costanzo and coworkers is important as a modification method for interlayer surfaces, but the procedure is tedious and analysis of results is complicated. The method of Raythatha and Lipsicas is preferable for an intermediate because of ease of preparation, but the infrared (IR) analysis and intercalation behavior of the hydrate are unknown.

Hydrated kaolinite is better suited to study intercalation behavior in kaolin minerals than hydrated halloysite because of fewer structural defects and less morphological variety. In the present study, hydrated kaolinite was prepared in accordance with the method of Raythatha and Lipsicas and then characterized. Using this hydrate as an intermediate, the intercalation behavior of amino acids was investigated in detail.

EXPERIMENTAL

Materials

The kaolinite used was low-defect kaolinite from Georgia (KGa-1). The kaolinite was washed repeatedly to eliminate soluble impurities (<2 μm).

Preparation of hydrated kaolinite

A Kao-DMSO intercalate was prepared by the method of Olejnik *et al.* (1968). For preparation of hydrated kaolinite a Kao-DMSO intercalate was reacted for 300 h. The extent of intercalation, as deter-

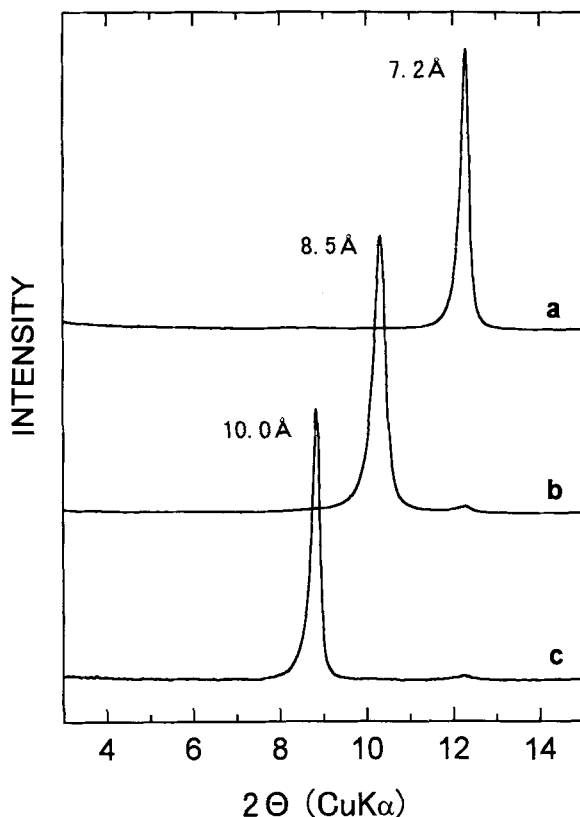


Figure 1. Powder X-ray diffraction patterns for (a) kaolinite, (b) 8.5-Å hydrated kaolinite, and (c) 10.0-Å hydrated kaolinite.

mined by the relative $d(001)$ -peak intensities of the intercalated and non-intercalated phases, was 93–94%.

Hydrated kaolinite was obtained by the method of Raythatha and Lipsicas (1985) as follows: the Kao-DMSO intercalate was washed by centrifugation with methyl alcohol 20–30 times and then with water (below 20°C) 5–10 times. From this, two well-crystallized hydrated kaolinites, a 10.0-Å and an 8.5-Å hydrate, were obtained. A small amount of residual 7.2-Å kaolinite phase, however, was always present. The 10.0-Å hydrate occurs only in the presence of water and quickly changes to the 8.5-Å hydrate on air-drying. When a suspension of the 10.0-Å hydrate was heated to temperatures >30°C, the hydrated phase generally partially collapsed to the 7.2-Å kaolinite phase. The 8.5-Å hydrate was apparently stable in air, whereas on addition of water, it reverted gradually to the 10.0-Å hydrate. The composition of the 8.5-Å hydrate was determined by differential thermal analysis (DTA) and thermogravimetric analysis (TG). The hydrated kaolinite used for the intercalation of amino acids was stored in a refrigerator as a 3% suspension. The pH of this suspension was ~5.4–5.7.

Intercalation of amino acid into hydrated kaolinite

Amino acids used in this study were glycine (Gly, carbon-number: $N_c = 2$) and a series of ω -amino acids having normal carbon chains: β -alanine (β -Ala, $N_c = 3$), γ -aminobutyric acid (γ -Aba, $N_c = 4$), δ -aminovaleic acid (δ -Ava, $N_c = 5$) and ϵ -aminocaproic acid (ϵ -Aca, $N_c = 6$).

In most cases, the intercalate of hydrated kaolinite (KH) with amino acid (KH-amino acid) was obtained by using solutions with pH values near the isoelectric point as follows: appropriate amounts of hydrated kaolinite suspension were mixed with predetermined amounts of amino acid solution of various concentrations, keeping the total volume to 50 mL per 1 g of kaolinite. The mixtures were shaken at 25°C for 48 h, after which the product was spontaneously precipitated or centrifuged, and then subjected to powder X-ray diffraction (XRD) measurement in a wet state. The centrifuged product and its washed product were further submitted for XRD, DTA-TG, and IR spectroscopy measurements after drying at various conditions. A mixture of kaolinite and amino acid (Kao-amino acid) was also obtained by using a kaolinite suspension which contained kaolinite in parts equal to that in the hydrated kaolinite suspension. For Gly and β -Ala, intercalation was performed in solutions adjusted to various pH values (0.5–13.5) with HCl or NaOH to investigate the effect of pH.

The intercalates were unstable when washed in water. Therefore, for convenience, the amount of intercalated amino acid was calculated from the DTA-TG data by subtracting the amino acid content in the mixture from that in the intercalate. Thus, the amount of amino acid bound to the external surfaces of the particles of intercalate was assumed to be equal to the amino acid content of the mixture. The ideal formula of kaolinite, $Al_2Si_2O_5(OH)_4$, was assumed to be the composition of the sample.

Apparatus

XRD powder patterns were recorded on a Rigaku diffractometer Rad-C system using $CuK\alpha$ radiation (40 KV-140 mA) and a graphite monochromator. IR spectra were obtained using a JASCO IR-700 spectrophotometer by the KBr absorption method. DTA-TG measurements were made on a Rigaku TAS-100 system (10°C/min, in air).

RESULTS

Characterization of hydrated kaolinite

Figure 1 shows the XRD patterns of the starting kaolinite (a), the 8.5-Å hydrate (b), and the 10.0-Å hydrate (c). The (001) peak profiles of both hydrated phases were sharp and peaks to $l = 5$ were observed.

Figure 2 illustrates the IR spectra of the kaolinite and the 8.5-Å hydrated kaolinite in the OH-stretching

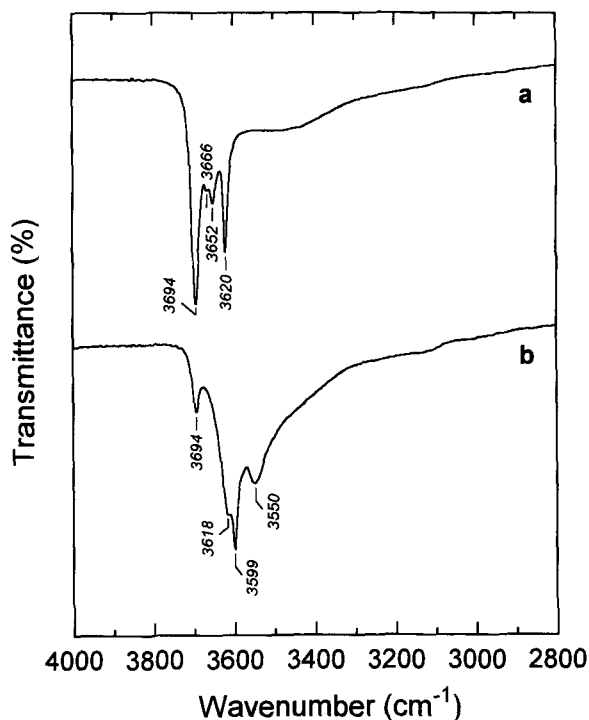


Figure 2. IR spectra for (a) kaolinite and (b) 8.5-Å hydrated kaolinite.

region. For the 8.5-Å hydrated kaolinite, the bands at 3694, 3666, and 3652 cm^{-1} are attributed to the inner-surface hydroxyls in the 1:1 layer (Farmer and Russell, 1964; Rouxhet *et al.*, 1977) and were reduced in intensity. In contrast, the band at 3620 cm^{-1} owing to the inner hydroxyl displayed little change. Additional bands at 3599 and 3550 cm^{-1} are due to the OH-stretching vibrations of intercalated H_2O and loosely bonded H_2O , respectively (Costanzo *et al.*, 1984b; Frost and Kristof, 1997).

In the low-frequency region (not shown), the band at 938 cm^{-1} owing to the Al-OH deformation vibration of the inner-surface hydroxyls (Farmer and Russell, 1964) was reduced in intensity and an additional small band at 967 cm^{-1} appeared. This result may correspond to the interaction between the intercalated H_2O and the OH of the kaolinite surface. A similar result was observed by Wada (1965) and Tunney and Detellier (1994).

Tunney and Detellier (1994) prepared a Kao-ethylene glycol intercalate using a Kao-DMSO intercalate as an intermediate, and then obtained 10.0-Å and 8.4-Å hydrated kaolinites by washing the Kao-ethylene glycol intercalate with water. They noted two IR spectra for their 8.4-Å hydrate. In one case, associated with the appearance of the 3599- cm^{-1} band, the 940- cm^{-1} band shifted to 968 cm^{-1} and the broad bending-vibration band of H_2O occurred at 1647 cm^{-1} . In the other case, the 968 and 3599- cm^{-1} bands did not occur,

and the H_2O -bending band occurred at 1655 cm^{-1} . The appearance of two spectra was attributed to heterogeneity in the sample. The IR spectrum of the 8.5-Å hydrate in the present study was similar to the 8.4-Å hydrate of Tunney and Detellier. A spectrum similar to that of the latter was sometimes observed when hydrated kaolinite was prepared by washing Kao-DMSO intercalate with water above 30°C, or a hydrate suspension was left at temperatures above 30°C for periods >1 wk.

The IR spectrum of the 8.4-Å hydrate obtained by Costanzo and Giese (1990) differs from those of the hydrates here and of Tunney and Detellier. This may be related to differences in interlayer bonding between the two hydrates, as discussed by Tunney and Detellier.

No bands owing to DMSO were observed in the IR spectrum of the hydrated kaolinite, showing the hydrate is free from DMSO residue. The composition of the 8.5-Å hydrate was determined to be $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 0.81\text{H}_2\text{O}$ from DTA-TG data.

Intercalation of amino acids

Powder X-ray diffraction. The intercalation of amino acids near the isoelectric point depended on the concentration and the carbon number of the amino acid. Almost all the 10.0-Å hydrated phase converted to the intercalated phase in solutions more concentrated than 0.5–1 M for Gly, 2–3 M for β -Ala, and 12 M for γ -Aba and δ -Ava. The $d(001)$ -values of the fully intercalated phases were 10.3 Å for Gly, 11.8 Å for β -Ala, 12.0 Å for γ -Aba, and 14.4 Å for δ -Ava. However, a small amount of residual kaolinite phase was always observed as well as the hydrated kaolinite. ϵ -Aca having a longer carbon chain was only partially intercalated even in a saturated solution (~ 7 M). The intercalation reaction attained equilibrium within 24 h and no further changes were observed.

Figure 3 shows the XRD patterns of KH-amino acid intercalates after air-drying for 48 h (26–28°C, $\sim 60\%$ relative humidity). The (001) reflections of the intercalates of Gly, β -Ala, and γ -Aba are sharp and the high order reflections to $l = 5$ –6 were observed. The percent of intercalation, as judged by the relative (001) peak intensities of the intercalated and non-intercalated phases, was >93% for these intercalates. The δ -Ava intercalate also showed high-order reflections to $l = 6$, although the (001) reflection was broader.

Table 1 shows the d -values and the Δ -values ($\Delta = \text{interlayer thickness} = d(001) - 7.2 \text{ \AA}$) of the amino acid intercalates. The $d(001)$ -values of the intercalates of Gly, β -Ala, and γ -Aba (12.0-Å phase) changed little under various drying conditions, whereas the $d(001)$ -values of the δ -Ava intercalates varied stepwise with drying conditions: 14.4 to 12.4 to 12.1 Å. These phase transformations were reversible, and occurred quickly with variations in humidity. Similar transitions were

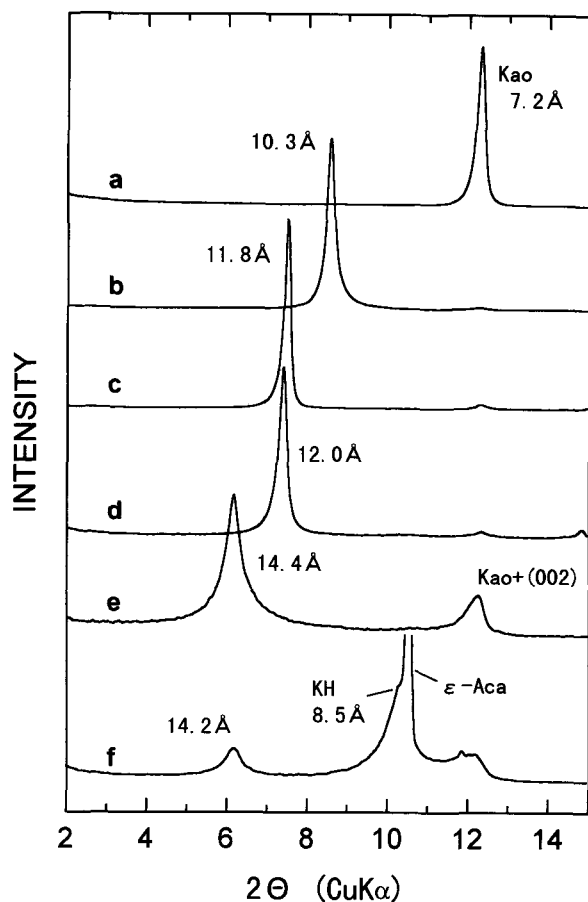


Figure 3. Powder X-ray diffraction patterns for kaolinite and the KH-amino acid intercalates centrifuged and air-dried for 24 h: (a) kaolinite, (b) KH-Gly intercalate, (c) KH- β -Ala intercalate, (d) KH- γ -Aba intercalate, (e) KH- δ -Ava intercalate, and (f) KH- ϵ -Aca intercalate.

also observed in the ϵ -Aca intercalate. The (001) peaks of the δ -Ava and ϵ -Aca intercalates broadened under vacuum or upon heating.

For γ -Aba, the 13.0-Å intercalated phase occurred in solutions at concentrations of 2–12 M and coexisted with the 12.0-Å phase. This 13.0-Å phase may be an intermediate phase in which more H₂O is intercalated or molecules vary in orientation.

A small quantity of hydrated kaolinite suspension was mixed with a 0.1–1 M amino acid solution at the ratio of 50–150 mL to 1 g of kaolinite. The mixture was then air-dried with occasional stirring. This allowed the intercalate to form using a dilute initial solution. The minimum amounts of amino acids required to form fully intercalated phases were: 2–3 moles for Gly, 3–4 moles for β -Ala, 3–6 moles for γ -Aba, and 6–10 moles for δ -Ava per Si₂Al₂O₅(OH)₄. This method, however, produces some inhomogeneities of intercalation in the sample.

Thermal analysis. Figure 4 shows the DTA-TG curves for kaolinite (a), the KH-Gly intercalate (b), and KH- β -Ala intercalate (c). In the DTA curve for the KH-Gly intercalate, the low-temperature exotherm occurs at 215–285°C, although Gly alone showed an endotherm by melting and decomposition at 250°C. A similar exotherm also appeared in the corresponding Kao-Gly mixture (not intercalated). No peak distinctly attributed to the decomposition of the intercalated Gly occurred between 200–340°C.

The endotherms at 200–215 and 326°C in the KH- β -Ala intercalate were also observed in the Kao- β -Ala mixture. β -Ala alone showed endotherms at 206 and 330°C. The endotherm at 230–270°C in the intercalate, which is not observed in the mixture, is attributed to the decomposition of the intercalated β -Ala molecules.

Table 1. The $d(001)$ -value and the Δ -value of the KH-amino acid intercalates under various conditions.

Amino acid	Drying condition									
	In solution		Air-dried ¹		On silica gel ²		At 80°C ³		At 80°C <i>in vacuo</i> ⁴	
	$d(001)$	Δ	$d(001)$	Δ	$d(001)$	Δ	$d(001)$	Δ	$d(001)$	Δ
Gly	10.3	3.1	10.3	3.1	10.3	3.1	10.3	3.1	10.2	3.0
β -Ala	11.8	4.6	11.8	4.6	11.8	4.6	11.8	4.6	11.8	4.6
γ -Aba	12.0 ⁵	4.8	12.0	4.8	12.0	4.8	12.0	4.8	12.0	4.8
δ -Ava	14.4	7.2	14.4	7.2	14.4	7.2	12.4	5.2	12.1	4.9
					12.4	5.2				
ϵ -Aca	14.2	7.0	14.2	7.0	13.2	6.0	12.5 ⁸	5.3	12.5 ⁸	5.3

¹ Air-dried for 48 h (~26–28°C, ~55–60% relative humidity).

² Dried on silica gel for 48 h after air-drying.

³ Dried at 80°C for 24 h after air-drying.

⁴ Dried at 80°C *in vacuo* for 24 h after air-drying.

⁵ Phase appeared in solutions of concentrations >4 M.

⁶ Phase appeared in solutions of 2–10 M.

⁷ Phase appeared temporarily in the drying process.

⁸ Phases showed very diffused (001) peaks.

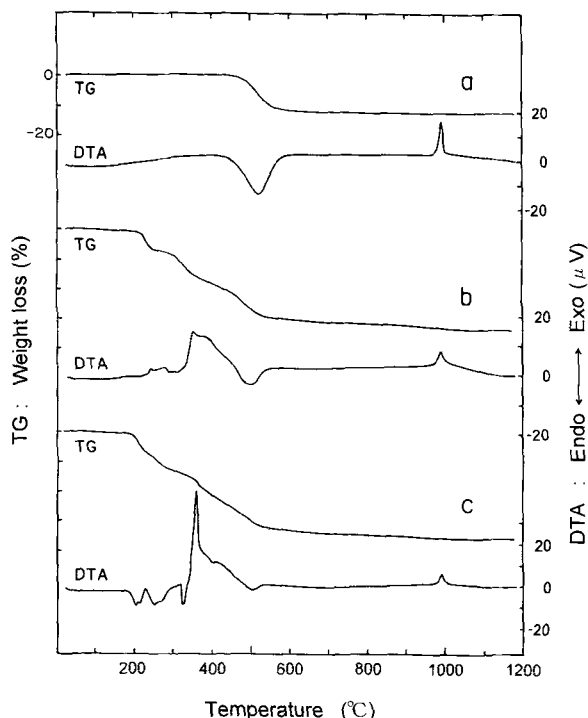


Figure 4. DTA-TG curves for (a) kaolinite, (b) KH-Gly intercalate, and (c) KH- β -Ala intercalate.

The compositions of the Gly and β -Ala intercalates were determined to be $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{Gly})_{0.67}\cdot 0.24\text{H}_2\text{O}$ and $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\beta\text{-Ala})_{0.63}\cdot 0.25\text{H}_2\text{O}$, respectively, from the TG data.

Effect of pH. The KH-Gly intercalate (10.3 Å) and the KH- β -Ala intercalate (11.8 Å) generally occur in the pH range of pK_1 ($-\text{COO}^-$: 2.34 for Gly; 3.55 for β -Ala) to pK_2 ($-\text{NH}_3^+$: 9.60 for Gly; 10.24 for β -Ala). The conversion of the hydrated phase to the intercalated phase occurred even near pK_1 or pK_2 in solutions of high concentration (>2 M), but only near the isoelectric point ($\text{pI} = 5.95$ for Gly, 6.95 for β -Ala) in dilute solutions. This indicates that intercalation depends on the concentration of zwitterion, since the amino acid exists predominantly as a zwitterionic form ($\text{NH}_3^+\text{RCOO}^-$) near the isoelectric point.

In the pH range below pK_1 or above pK_2 , it became more difficult for intercalation to occur. At high concentrations (>1 – 2 M), however, several other intercalated phases with larger $d(001)$ -values occurred partially, in addition to the 10.3-Å or 11.8-Å phase. Since most of these phases are unstable in ambient air, they are probably phases where amino acid or its salt is intercalated with H_2O . These phases are currently being investigated.

Infrared spectroscopy. The IR spectra of kaolinite, Gly, β -Ala, the Kao-Gly and Kao- β -Ala mixtures, and the KH-Gly and KH- β -Ala intercalates are given in

Figure 5. The mixtures and the intercalates were obtained from solutions with pH values near the isoelectric point.

KH-Gly Intercalate. The IR spectrum for the Kao-Gly mixture showed no changes in the OH-stretching region confirming that intercalation did not occur, consistent with the XRD data (Figure 5A, trace d). In contrast, the inner-surface OH-stretching bands at 3694, 3666, and 3652 cm^{-1} were reduced in intensity and additional bands at 3626 cm^{-1} occurred in the KH-Gly intercalate (Figure 5A, trace e). The 3626- cm^{-1} band may be a result of hydrogen bonding between the inner-surface hydroxyls and Gly molecules. The 3694- cm^{-1} band in kaolinite shifted to a slightly higher frequency, 3697 cm^{-1} , in the intercalate. In general, the 3620- cm^{-1} band owing to the inner hydroxyl is not affected on intercalation (Cruz *et al.*, 1973). This band is superposed over the 3626- cm^{-1} band and occurs as a shoulder in the intercalate. The broad bands at 3588 and 3414 cm^{-1} are presumably due to the OH-stretching vibrations of strongly and weakly bonded H_2O .

In the low-frequency region (Figure 5C, trace e), the band at 938 cm^{-1} , owing to the Al-OH deformation vibration, was reduced in intensity, corresponding to a perturbation of the inner-surface hydroxyl by Gly in the OH-stretching region. The bands at 795 and 789 cm^{-1} also decreased in intensity. Anton and Rouxhet (1977) attributed similar intensity decrease in Kao-DMSO intercalate to a perturbation of the vibrations involving octahedral cations and hydroxyls by DMSO. Further, the band at 540 cm^{-1} assigned to Si-O-Al skeletal vibration (Farmer and Russell, 1964) decreased in intensity and a shoulder occurred near 560 cm^{-1} . Anton and Rouxhet (1977) also observed the shift to 550 cm^{-1} of the 540- cm^{-1} band in the Kao-DMSO intercalate and attributed this shift to a perturbation of the coordination sphere of Al ions by DMSO. The shift of the 540- cm^{-1} band in the Gly intercalate may result from a similar perturbation.

The perpendicular and in-plane Si-O stretching bands at 1104, 1032, and 1008 cm^{-1} in kaolinite occurred at 1127, 1091, 1050, 1031, and 1009 cm^{-1} in the intercalate (Figure 5C, trace e). Olejnik *et al.* (1971) observed a splitting of the perpendicular vibration and shifts of the in-plane vibrations on intercalation of dimethyl-acetamide in kaolinite. They noted that these changes may occur because intercalation and separation of the lamellae affected the orientation of the crystals, the regularity of crystal structure, the crystal size, and the dielectric constant of the medium. Intercalation of Gly also causes a splitting and shifts of Si-O vibrations.

Gly molecules exist as zwitterionic forms, $\text{NH}_3^+\text{CH}_2\text{COO}^-$, both in solution near the isoelectric point ($\text{pI} = 5.95$) and in the crystalline state (Meister, 1965; Laulich *et al.*, 1966). The IR spectra of Gly are given

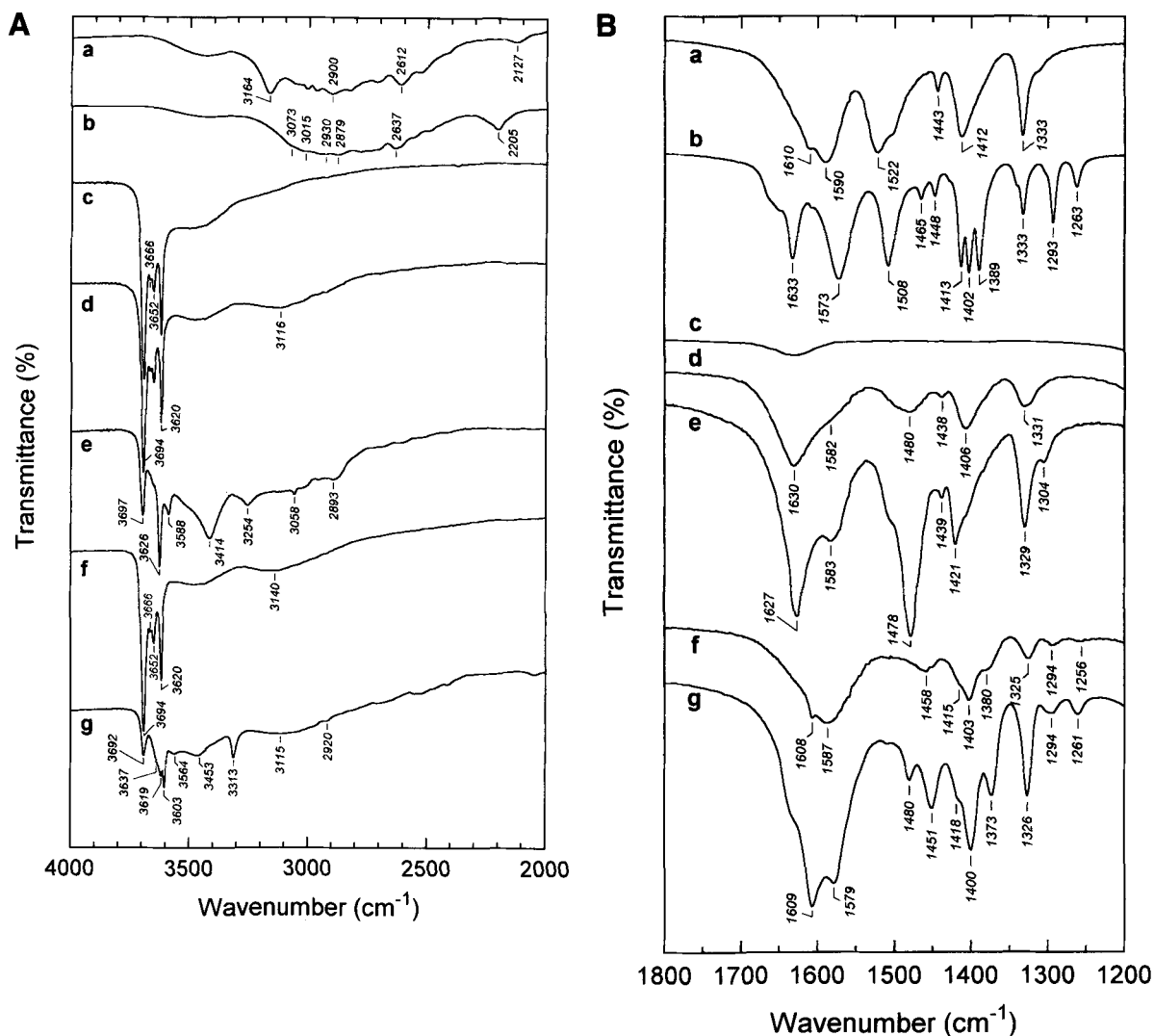


Figure 5. A) IR spectra in the 4000–2000 cm⁻¹ region for (a) Gly, (b) β -Ala, (c) kaolinite, (d) Kao-Gly mixture, (e) KH-Gly intercalate, (f) Kao- β -Ala mixture, and (g) KH- β -Ala intercalate; B) IR spectra in the 1800–1200 cm⁻¹ region for (a) Gly, (b) β -Ala, (c) kaolinite, (d) Kao-Gly mixture, (e) KH-Gly intercalate, (f) Kao- β -Ala mixture, and (g) KH- β -Ala intercalate.

in Figure 5A, trace a, 5B, trace a, and 5C, trace a. On intercalation, the absorptions of Gly were considerably changed (Figure 5A, trace e, 5B, trace e, and 5C, trace e). The vibrational assignments of the strong bands for Gly and the intercalated Gly are given in Table 2. The assignments for Gly are based on those of Tsuboi *et al.* (1963), Laulich *et al.* (1966), and Uvdal *et al.* (1990).

Intercalation of Gly occurred more readily near the isoelectric point. Gly is thus expected to be intercalated as a zwitterion. Indeed, in the intercalate, neither stretching bands near 1740–1730 and 1260–1235 cm⁻¹ owing to the COOH group (Tsuboi *et al.*, 1963; Pearson and Slifkin, 1972) nor stretching bands near 3400–3380 cm⁻¹ owing to the non-ionic NH₂ group (Svatos *et al.*, 1955) were observed. Instead, the intercalate

showed a band at 1478 cm⁻¹ owing to symmetric NH₃⁺-deformation vibration and a band at 1421 cm⁻¹ owing to symmetric COO⁻-stretching vibration (Figure 5A, trace e and 5B, trace e). Near 1600 cm⁻¹, bands owing to asymmetric NH₃⁺-deformation vibration and asymmetric COO⁻-stretching vibration are superposed. The absorption of excess Gly and water was not considered significant. Although detailed assignments of these bands are difficult to make, the following observations are noted.

The spectrum of the Kao-Gly mixture in the 1800–1200 cm⁻¹ region, which was obtained near the isoelectric point, was similar to that of the intercalate except that the bands were weaker and the bands at 1627, 1583, 1478, and 1421 cm⁻¹ in the intercalate occurred at 1630, 1582, 1480, and 1406 cm⁻¹ in the mixture

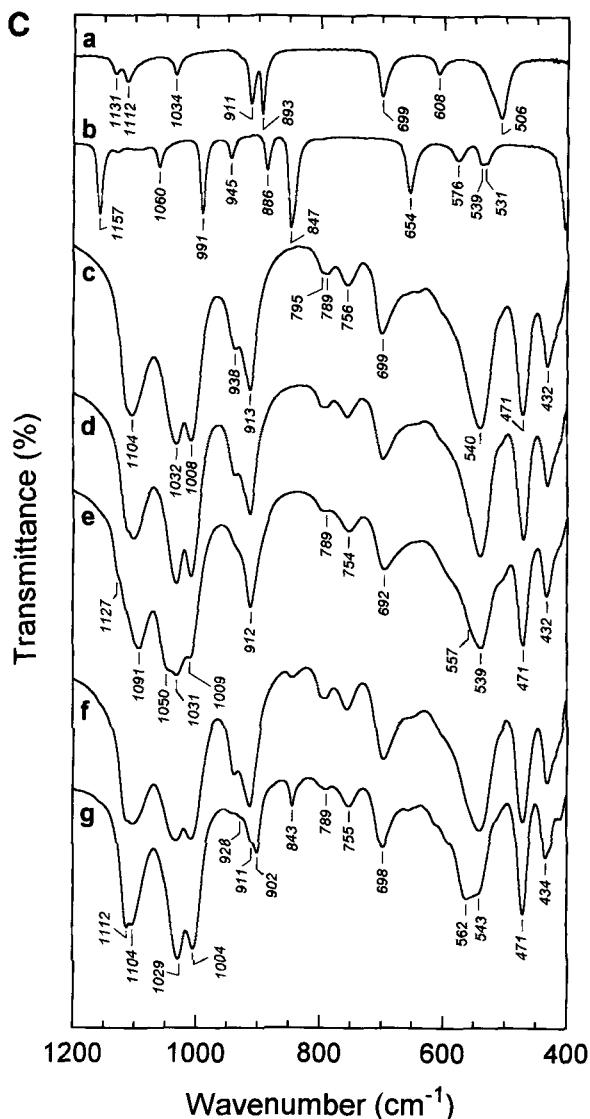


Figure 5. Continued. C) IR spectra in the 1200–400 cm⁻¹ region for (a) Gly, (b) β-Ala, (c) kaolinite, (d) Kao-Gly mixture, (e) KH-Gly intercalate, (f) Kao-β-Ala mixture, and (g) KH-β-Ala intercalate.

(Figure 5B, trace d). These bands are attributed to Gly molecules adsorbed on the external surfaces (edges or faces) of particles. However, in the Kao-Gly mixture obtained from a solution of pH < 1 (data not shown), a shoulder near 1580 cm⁻¹ did not occur. Based on the appearance of a weak band near 1740 cm⁻¹, the presence of COOH in this mixture is assumed. The bands near 1630 and 1480 cm⁻¹ in both mixtures are attributed to the asymmetric and symmetric NH₃⁺-deformation vibrations. On the other hand, in the Kao-Gly mixture obtained from a solution of pH > 12 (data not shown), a band near 1630 cm⁻¹ did not occur, but bands occurred near 1595 and 1567 cm⁻¹. These bands

are attributed to the NH₂-scissor vibration and asymmetric COO⁻-stretching vibration, respectively.

The 1627-cm⁻¹ and 1583-cm⁻¹ bands in the intercalate are assigned to the asymmetric NH₃⁺-deformation vibration and the asymmetric COO⁻-stretching vibration of the intercalated Gly in the zwitterionic form. In the spectrum for the KH-Gly intercalate, bands owing to Gly adsorbed on the external surfaces of particles and bands owing to the intercalated Gly are superposed. However, the amount of Gly adsorbed on external surfaces is small compared to that of intercalated Gly. Therefore, the spectrum for the intercalate principally reflects the interaction between Gly molecules and the interlamellar surfaces of kaolinite. The mechanism of interaction between Gly molecules and external surfaces requires further study.

In Figure 5A, trace a, the broad and strong absorption band between 3300–2300 cm⁻¹ occurs in most amino acids in the crystalline (zwitterionic) state and is characteristic of the intermolecular hydrogen-bonding, COO⁻ ··· NH₃⁺ (Uvdal *et al.*, 1990). In the Gly intercalate, several of these strong bands were shifted to 3300–2800 cm⁻¹ (Figure 5A, trace e). The small band at 3254 cm⁻¹ is assigned to the asymmetric NH₃⁺-stretching vibration. This band position is higher than that of the NH₃⁺ group of Gly in the crystalline state, 3164 cm⁻¹.

KH-β-Ala Intercalate. The bands at 3694, 3666, and 3652 cm⁻¹ in kaolinite were significantly reduced in intensity as in the KH-Gly intercalate, and an additional band occurred at 3637 cm⁻¹ (Figure 5A, trace g). This band is attributed to the hydrogen bonded inner-surface hydroxyls. The 3694-cm⁻¹ band shifted little in the intercalate. The band at 3603 cm⁻¹ is attributed to the OH-stretching vibration of intercalated and non-bonded H₂O, and the bands at 3564 and 3453 cm⁻¹ to that of more strongly and weakly bonded H₂O, respectively.

In the low-frequency region (Figure 5C, trace g), both the 938-cm⁻¹ and 913-cm⁻¹ bands owing to the Al-OH deformation vibrations were reduced in intensity, and an additional band occurred at 928 and 902 cm⁻¹. The shift of the 938-cm⁻¹ and 913-cm⁻¹ bands to lower frequencies may suggest reduced hydrogen bonding of Al-OH. Furthermore, like the Gly intercalate, the bands at 795, 789 and 540 cm⁻¹ were reduced in intensity and an additional band occurred at 562 cm⁻¹. In the Si-O stretching region, a slight intensity decrease of the 1112-cm⁻¹ band and a shift of the 1032-cm⁻¹ and 1008-cm⁻¹ bands to 1029 and 1004 cm⁻¹ were observed.

The IR spectra of β-Ala in its zwitterionic form are shown in Figure 5A, trace b, 5B, trace b, and 5C, trace b, and the assignments of the strong bands of β-Ala and the intercalated β-Ala are listed in Table 2. There are no generally accepted assignments of β-Ala. Here,

Table 2. The position of the strongest peaks and their assignments in the IR spectra of crystalline glycine and intercalated glycine, and crystalline β -alanine and intercalated β -alanine.

Crystalline glycine	Intercalated glycine	Assignments	Crystalline β -alanine	Intercalated β -alanine	Assignments
3164	3254	NH ₃ ⁺ asym. str. NH ₃ ⁺ asym. str.		3313 3115	NH ₃ ⁺ asym. str. NH ₃ ⁺ sym. str.
	3058		3073 3015	3056	
2900	2893	CH ₂ asym. str.	2930 2879	2920	CH ₂ str. CH ₂ str.
2820		CH ₂ sym. str.			
1610	1627	NH ₃ ⁺ asym. def.	1633	1609	NH ₃ ⁺ asym. def.
1590	1583	COO ⁻ asym. str.	1573	1579	COO ⁻ asym. str.
1522	1478	NH ₃ ⁺ sym. def.	1508 1465	1480	NH ₃ ⁺ sym. def. CH ₂ def. scissor CH ₂ def. scissor
1443	1439	CH ₂ def. scissor	1448	1451	CH ₂ def. scissor
1412	1421	COO ⁻ sym. str.	1413	1418	COO ⁻ sym. str. (+ CH ₂ def.)
			1402	1400	COO ⁻ sym. str. (+ C _{β} C str.)
			1389	1373	COO ⁻ sym. str. (+ CH ₂ def. + ν C _{β} C)
1333	1329	CH ₂ def. wag. + C-C	1333	1326	CH ₂ def. wag.
1314		CH ₂ twist.	1293	1294	CH ₂ twist.
			1263	1261	NH ₃ ⁺ rock.
			1157	1157	CH ₂ def. rock.
1131		NH ₃ ⁺ rock.	1128		NH ₃ ⁺ rock.
1034		C-N str.	1064		C-N str.

Note: asym./sym., asymmetric/symmetric; str., stretching; def., deformation; wag./twist/rock., wagging/twisting/rocking.

the assignments are those by Garrigou-Lagrange (1978) and Berezhinskii *et al.* (1998).

For the KH- β -Ala intercalate, no bands were observed for the COOH group, but symmetric COO⁻-stretching bands occurred at 1418–1373 cm⁻¹. The band at 1633 cm⁻¹ was reduced in intensity. A strong band occurred at 1609 cm⁻¹ and this band formed a combined broad band with a strong 1579-cm⁻¹ band (Figure 5B, trace g). The bands owing to the intercalated β -Ala were assigned by comparison with the Kao- β -Ala mixture, *e.g.*, KH-Gly intercalate. Thus, the bands at 1609 and 1480 cm⁻¹ were attributed to the asymmetric and symmetric NH₃⁺-deformation vibrations, respectively, and the band at 1579 cm⁻¹ to the asymmetric COO⁻-stretching vibration. In the NH-stretching region, the broad and strong absorption band occurred between 3200–2800 cm⁻¹ (Figure 5A, trace g). The 3313-cm⁻¹ band may be due to the NH₃⁺-stretching vibration. The band positions of the NH₃⁺-deformation vibrations were lower than those of the NH₃⁺ group of β -Ala in the crystalline state, and those of the asymmetric COO⁻-stretching vibrations and the NH₃⁺-stretching vibrations were higher. These results indicate that β -Ala is also intercalated as a zwitterionic form.

Deintercalation and reintercalation of amino acid

The intercalated amino acids were released by water washing. The intercalated phase of hydrated kaolinite showed a 10.0-Å peak in the XRD patterns after five or six washings of Gly and β -Ala intercalates and after

one or two washings of γ -Aba, δ -Ava, and ϵ -Aca intercalates. Figure 6 shows the IR spectra for the KH- β -Ala intercalate before and after water washing. The bands at 3637 and 3313 cm⁻¹ do not occur after washing. Also, the bands at 3603, 3564, and 3453 cm⁻¹ owing to OH-stretching vibrations of H₂O do not occur, but bands at 3599 and 3550 cm⁻¹ do. The IR spectra for the washed intercalates were nearly identical to the spectrum of the 8.5-Å hydrated kaolinite (Figure 6, trace d). Since the KH-Gly and KH- β -Ala intercalates include less water than the hydrated kaolinite, this result suggests that H₂O molecules diffuse into the interlayer during the process of deintercalation of amino acid molecules.

A re-hydrated kaolinite showed a broad (001) XRD reflection, indicating loss of crystallinity. However, when reacted again with an amino acid solution, the hydrate easily intercalates amino acids, especially Gly and β -Ala. The XRD pattern of the product showed an ordered structure, similar to the initial one.

DISCUSSION

The NH₃⁺-stretching frequencies of Gly and β -Ala shifted to higher frequencies on intercalation. Uvdal *et al.* (1990) reported that in a thin layer of Gly on a Cu substrate, the NH₃⁺-stretching vibration of zwitterionic Gly shifted to higher frequency, from 3169 to 3180 cm⁻¹. Jang and Condrate (1972) also observed that the NH₃⁺-stretching band occurred at 3220 cm⁻¹ in the H-montmorillonite-Gly intercalate and concluded that the intercalated Gly molecules involved less intermolecu-

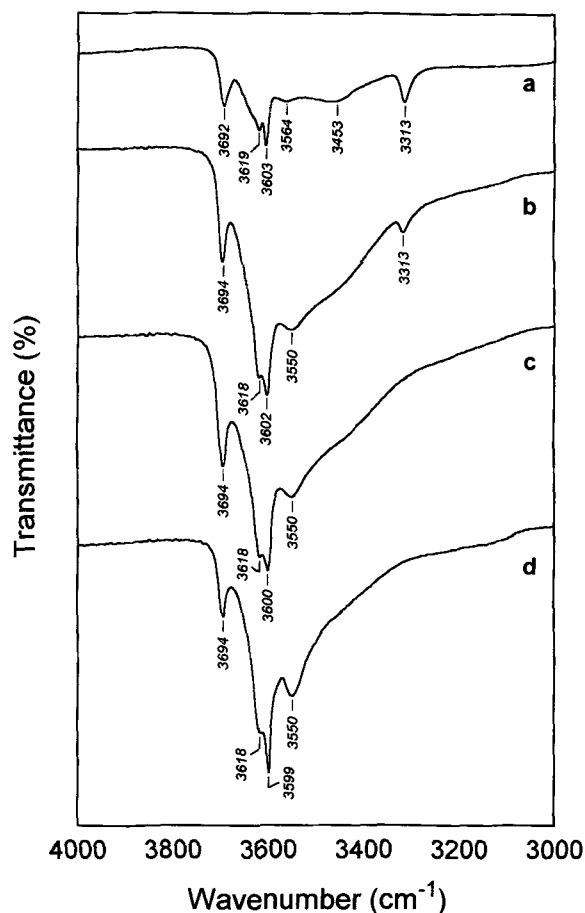


Figure 6. IR spectra for the KH- β -Ala intercalate: (a) unwashed, (b) washed two times, (c) washed 12 times, and (d) for the 8.5- \AA hydrated kaolinite.

lar hydrogen bonding and there was weaker interaction with surfaces.

A similar mechanism is assumed for the KH-amino acid intercalates. Amino acid in the crystalline (zwitterionic) state forms a strong $\text{NH}_3^+ \cdots \text{COO}^-$ intermolecular hydrogen bond between adjacent molecules. As a result, the NH_3^+ -stretching vibrations shift to lower frequencies and a broad absorption band occurs between 3300–2300 cm^{-1} . On intercalation, however, the strong intermolecular hydrogen bonding in the crystalline state may break and is replaced by a lower degree of interaction with surfaces in the intercalate. The overall effect of these interactions is a shift of the NH_3^+ -stretching bands to higher frequencies. These results are consistent with Kao-hydrazine and Kao-urea intercalates (Ledoux and White, 1966).

In general, the formation of hydrogen bonds shifts deformation vibrations to higher frequencies and stretching vibrations to lower frequencies (Serratosa *et al.*, 1970; Hadzi and Bratos, 1976). However, the shifts of the NH_3^+ -deformation bands and the COO^- -stretching bands in the Gly and β -Ala intercalates do not

follow the rule. Although the reason for each band shift cannot be clarified from the present IR data, the shift of the symmetric NH_3^+ bands to 1480 cm^{-1} , together with the shift of the NH_3^+ -stretching bands to 3254 or 3313 cm^{-1} , may indicate that the hydrogen bonding of the NH_3^+ group in the amino acid intercalate is weaker than that of amino acids in the crystalline (zwitterionic) state.

An interaction of the NH_3^+ group with the inner Al-OH surfaces of kaolinite possibly occurs. However, the COO^- group of the amino acid may act as a proton acceptor to form $\text{COO}^- \cdots \text{HO-Al}$, as in the Kao-potassium acetate intercalate (Ledoux and White, 1966). Therefore, the NH_3^+ group probably prefers to interact with the Si-O surface as a proton donor.

On intercalation of potassium acetate into kaolinite or halloysite, the hydrogen bonding between the inner-surface hydroxyl and acetate ion causes a perturbed band at 3600–3605 cm^{-1} (Ledoux and White, 1966; Frost and Kristof, 1997). Because the OH-stretching bands occur at 3626 cm^{-1} in the Gly intercalate and at 3637 cm^{-1} in the β -Ala intercalate, there is a weaker interaction between the COO^- group and the Al-OH surface than between the acetate ion and the surface. These stretching bands also suggest that β -Ala has less interaction with the Al-OH surface than Gly.

Crystallographic data for amino acids were given by Marsh (1958), Jose and Pant (1965), Bodor *et al.* (1967), Steward *et al.* (1973), and Honda *et al.* (1990). On the basis of these data, minimum van der Waals length along the short axes of fully extended molecules is 4.1 \AA , and those along the long axes increase from 5.6 \AA for Gly to 11.4 \AA for ϵ -Aca. In the presence of water, intercalates showed Δ -values of 3.1 \AA for Gly, 4.6 \AA for β -Ala, 4.8 \AA for γ -Aba, 7.2 \AA for δ -Ava, and 7.0 \AA for ϵ -Aca. This stepwise increase in Δ -values with carbon number seems to relate to either odd numbers or even numbers of C in the amino acid chains. With drying, Δ -values of the δ -Ava and ϵ -Aca intercalates were reduced stepwise. The Δ -values decreased to 4.6–5.3 \AA after drying at 80°C *in vacuo* except for the Gly intercalate. Based on the IR data showing that NH_3^+ and COO^- groups interact with the Si-O and Al-OH surfaces, respectively, the amino acid molecules apparently form a mono-molecular arrangement with the alkyl chain tilting toward the layer at an angle related to the H_2O content.

The Δ -value of the KH-Gly intercalate, 3.0–3.1 \AA , is too small relative to the smallest van der Waals thickness of Gly, 4.1 \AA . Carr and Chih (1971) reported a Δ -value of 3.2 \AA for the halloysite-Gly intercalate. Such a small Δ -value is often observed in kaolinite intercalates and is interpreted as involving a “keying” effect (Theng, 1974, p. 239–284) where the Gly molecule fits partially in the layer surface.

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E-mail of corresponding author: sato@nmiri.city.nagoya.jp
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