Dynamics of Interlayer Cations in Tetramethylammonium-Saponite Studied by ^{1}H, ^{2}H NMR, and Electrical Conductivity Measurements

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We observed ^{1}H and ^{2}H NMR spectra, ^{1}H NMR spin-lattice relaxation times, and electrical conductivities of water-saturated and anhydrous tetramethylammonium(TMA)-saponites between 100 and 415 K. The very weakly bound cations produced narrow ^{1}H and ^{2}H NMR lines observed in both specimens down to 150 K. The temperature dependence of the ^{1}H NMR spin-lattice relaxation times in the water-saturated and anhydrous samples gave asymmetric minima attributable to the heterogeneous overall rotation and self-diffusion of the cations. The inhomogeneity of the cationic motions in the anhydrous TMA-saponite was greater than in the water-saturated one. From measurements of the electrical conductivity of anhydrous TMA-saponite a large anisotropic cation-diffusivity was concluded.

Key words: Saponite; Cation Dynamics; NMR; Electrical Conductivity; Intercalation.

Introduction

A characteristic property of layered clay minerals is the intercalation with various molecules and ions whose concentrations can be controlled in a wide range. Lagaly has investigated clay-organic reactions and established a conventional method to determine the cation exchange capacity and the charge heterogeneity of the clays by estimation of the basal spacing [1, 2]. The dynamics of interlayer cations and guest molecules is sensitively influenced by the environment in clay minerals. In fact, a wide variety of water environment in hydrated clays was found by dielectric relaxation measurements [3].

In the present study we have measured NMR and the electric conductivity of a synthetic saponite ($(\mathrm{TMA})_x\mathrm{Si}_{4-x}\mathrm{Al}_x\mathrm{Mg}_3(\mathrm{OH})_2\mathrm{O}_{10}$) intercalated with tetramethylammonium(TMA) cations in order to discuss details of TMA motions in the saponite and the environmental heterogeneity originating from the 2-dimensional structure as well as the random distribution of anionic centers in the clay wall. Because of its high symmetry, a TMA cation is convenient to identify its motional mode and suitable to discuss the inhomogeneous crystal field. We used a synthetic clay for NMR measurement because it is free from paramagnetic impurities [4 - 6].

Experimental

Synthetic Na-saponite, $\mathrm{Na}_{0.4}\mathrm{Si}_{3.6}\mathrm{Al}_{0.4}\mathrm{Mg}_3(\mathrm{OH})_2\text{-}\mathrm{O}_{10}$, a reference clay (JCSS-3501) of the Clay Science Society of Japan was employed as the starting material. TMA-saponite was prepared by the ordinary cation exchange method using a 2 mol dm^{-3} aqueous tetramethylammonium chloride solution. The suspension of the cation exchanged clay was filtered and washed by distilled water until the filtrate showed negative reaction for the $\mathrm{AgNO_3}$ test. The prepared specimen was dehydrated by vacuuming at room temperature for one day. A part of this specimen was sealed in glass sample tubes with He gas of *ca.* 20 mm Hg for the NMR measurement. Another part was saturated with $\mathrm{D_2O}$ under saturated vapour pressure at room temperature and sealed in sample tubes after admitting He gas of atmospheric pressure. The $\mathrm{D_2O}$ content in the $\mathrm{D_2O}$ saturated TMA-saponite was determined by measuring the weight loss at 600 °C to be *ca.* 14 molecules per cation. X-Ray powder diffraction was carried out for these specimens to determine the basal spacing. Differential thermal analysis (DTA) was also conducted on these specimens to investigate their phase behaviour.

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Tetramethylammonium-d_{12} saponite was prepared in a similar way using fully deuterated $(CD_3)_4NCl$. This clay was also divided into two parts; one was dehydrated under vacuum and the other was saturated with H_2O. These specimens were sealed in glass tubes with He gas for ^1H and ^2H NMR measurements.

X-Ray diffraction measurements were carried out with a Philips X'Pert PW3040/00 diffractometer using CuKα radiation at room temperature. ^1H and ^2H NMR spectra were measured with a Bruker MSL-300 NMR system at 120 - 300 K. The sample temperature was controlled within ±2 K and its accuracy was estimated to be about ±5 K. ^1H NMR T_1 was measured with Bruker SXP-100 and home-made spectrometers at ^1H Larmor frequencies 14.9 and 48.9 MHz, respectively, at 100 - 400 K. The evaluated error in T_1 was ±10 %.

The electrical conductivity was measured at 1 kHz by the two terminal method using a Yokogawa-Hewlett-Packard 4261A LCR meter at 300 - 415 K. The preferentially oriented films of the TMA-saponite were obtained by slow evaporation of an aqueous suspension of the clay [7] and dried *in vacuo*. The thickness of the film was determined with a micrometer caliper to be 0.17 ± 0.02 mm. Using these films, the conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$, parallel and perpendicular to the layer, respectively, were measured [8]. For the $\sigma_{\perp}$ measurement, undefined-shape films (*ca.* 4 mm^2) with carbon paste electrodes (Acheson Electrodag 199) were used. Rectangular (1 mm × 3 mm) films put in an epoxy matrix were used to measure $\sigma_{\perp}$ by employing electrically conducting adhesives (Aremco bond 525, silver paste) as electrodes.

Results and Discussion

Thermal Measurements

The DTA thermogram of D_2O saturated TMA-saponite showed three small endothermic peaks at 217 ± 1, 241 ± 1, and 292 ± 1 K, and a large endothermic one at 265 ± 2 K on heating from 120 K to room temperature. Upon cooling, the small peaks could not be observed, while the large one was recorded with a marked hysteresis. This anomaly is explainable by the freezing of water probably adsorbed on the surface or between the clay particles. The small transitions seem to be attributable to small rearrangements of water molecules or the cations. Upon heating above room temperature, a large endothermic peak, attributable to the desorption of D_2O from the clay, was observed above 305 K. On the other hand, anhydrous TMA-saponite showed no thermal anomaly in the range of 120 - 320 K.

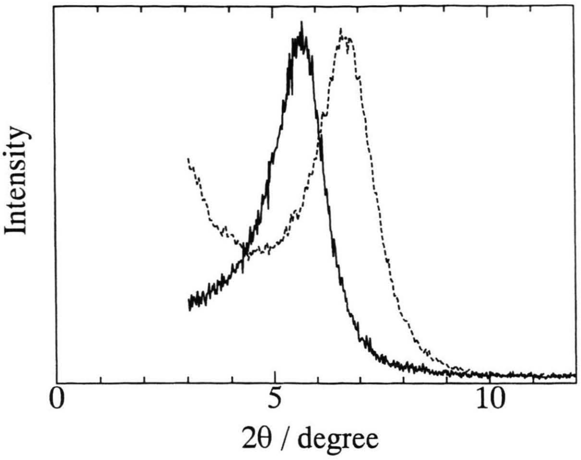

Fig. 1. X-Ray powder diffraction patterns of D_2O saturated (solid line) and anhydrous (broken-line) TMA-saponites measured at room temperature.

X-Ray Diffraction

X-Ray powder diffraction patterns of anhydrous and D_2O saturated TMA-saponites observed at room temperature are shown in Figure 1. The (001) *d*-spacings of 1.32 and 1.60 nm corresponding to the basal spacing of 0.36 and 0.64 nm were obtained [9] for anhydrous and D_2O saturated saponites, respectively. The increment of the basal spacing by hydration implies the swelling of the clay caused by D_2O absorption. The value of 0.36 nm in anhydrous TMA-saponite is much smaller than the cation diameter of 0.66 nm, evaluated from the typical C-N and C-H bond distances in methylamine and the van der Waals radius of hydrogen. This implies that the cations are located in the depressions formed on the surface of the clay wall [9]. The basal spacing of the anhydrous specimen was shown to be almost independent of temperature between room temperature and 450 K.

^2H and ^1H NMR Spectra

To investigate the cationic motion, we measured ^2H NMR spectra of anhydrous and H_2O saturated TMA-d_{12}-saponites. Figure 2 shows temperature dependences of the full width at half maximum ($\Delta\nu_{1/2}$) of ^2H absorption lines. The $\Delta\nu_{1/2}$ values in both compounds were only *ca.* 1.5 kHz even at 120 K indicating

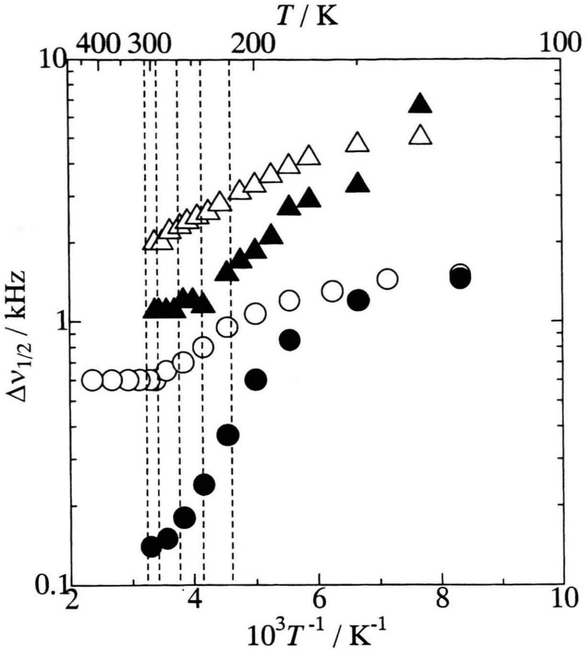

Fig. 2. Temperature dependences of the half-width ($\Delta\nu_{1/2}$) of NMR spectra: ^{1}H lines for D_2O saturated(closed triangles) and anhydrous(open triangles) TMA-saponites, and ^{2}H for H_2O saturated (closed circles) and anhydrous(open circles) TMA-d_{12}-saponites. The dashed lines indicate the temperatures of thermal anomalies observed by DTA.

the onset of isotropic rotation of the TMA-cations at low temperatures. The further reduction of the linewidth observed in both specimens between 200 and 300 K is attributable to thermal accelaration of translational motions of TMA-cations, such as jumping to neighbouring vacant sites.

^{1}H NMR spectra in D_2O saturated and anhydrous TMA-saponites also showed narrow linewidths less than 7 kHz above 130 K (Figure 2). This indicates the onset of the isotropic motion of TMA-cations [10] in the low-temperature range as shown from the ^{2}H NMR spectra. The observation of any ^{14}N NMR spectra should be expected, if the isotropic rotation could average the electric field gradient at the nuclei. But we could not obtain a ^{14}N signal implying that the residual electric field gradient from the layer charge centres seems to contribute significantly to the width.

^{1}H NMR Relaxation Time (T_1)

To explore details of cationic motions, we measured the temperature and frequency dependences of the ^{1}H NMR spin-lattice relaxation times (T_1) in D_2O saturated and anhydrous TMA-saponites.

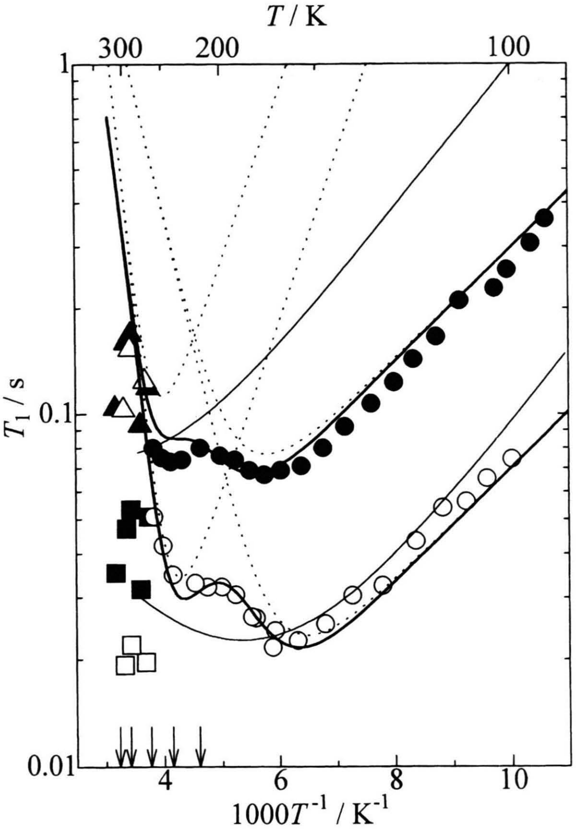

Fig. 3. Temperature and frequency dependences of ^{1}H NMR T_1 for D_2O saturated TMA-saponite observed at 14.9 MHz (open circles) and 48.9 MHz (closed circles) in which the long and short T_1 values observed above 265 K are shown by triangles and squares, respectively. Bold solid and dotted lines are the best-fitted theoretical curves. The calculated values using the BPP-formula are shown by thin solid lines. Arrows represent the temperatures of thermal anomalies observed by DTA.

D_2O saturated TMA-Saponite

^{1}H NMR relaxation measurements on D_2O saturated TMA-saponite performed below 265 K gave a single T_1 component and showed two minima around 160 and 240 K, which are assignable to some cationic motions (cf. Fig. 3). Hereafter, we call the motions giving rise to these minima at the low and high temperatures as mode **1** and **2**, respectively. The net relaxation rate is then represented by

$$(T_1)^{-1}_{\text{net}} = (T_1)^{-1}_{\text{mode }\mathbf{1}} + (T_1)^{-1}_{\text{mode }\mathbf{2}}. \tag{1}$$

For the relaxation due to a thermal motion which averages magnetic dipolar interactions between protons, we can apply the BPP equation [11]

$$T_1^{-1} = C\left[\frac{\tau}{1+\omega^2\tau^2} + \frac{4\tau}{1+4\omega^2\tau^2}\right]. \tag{2}$$

Here C, τ, and ω denote the motional constant, the correlation time of the motion, and the Larmor frequency, respectively. This equation predicts a ω^2 dependence of T_1 below the minimum as shown by thin solid lines in Fig. 3, whereas the observed T_1 given by the solid and open circles showed a much weaker frequency dependence of $\sim \omega^{1.0}$ below 140 K.

Similar anomalous frequency dependences of ^{1}H T_1 observed in various inhomogeneous systems, such as glasses [12] and intercalation compounds [13, 14], were explained by taking account of a continuous distribution of the correlation time τ. Since the crystal field around the interlayer cations in clay is expected to be highly anisotropic and inhomogeneous [1, 2], we can assume a distributed potential for the cationic rotation. Here we introduce a Cole-Davidson type distribution of τ [12, 15] given by

$$\begin{aligned} g(\tau) &= \frac{\sin\beta\pi}{\pi}\left(\frac{\tau}{\tau_{\text{c.o.}}-\tau}\right)^{\beta} \qquad \tau \le \tau_{\text{c.o.}}, \\ &= 0 \qquad\qquad\qquad\qquad\quad \tau > \tau_{\text{c.o.}}, \end{aligned} \tag{3}$$

where $\beta (0 < \beta \le 1)$ indicates the degree of distribution and $\tau_{\text{c.o.}}$ is the cut-off of the correlation time. The limiting case of $\beta = 1$ affords the usual single correlation time. Substituting the τ distribution given by (3) into (2), the relaxation rate is represented by

$$\begin{aligned} T_1^{-1} = C\Bigg[&\frac{\tau_{\text{c.o.}}\sin(\beta\tan^{-1}\omega\tau)}{\omega\tau_{\text{c.o.}}(1+\omega^2\tau_{\text{c.o.}}^2)^{\beta/2}} \\ &+ \frac{2\tau_{\text{c.o.}}\sin(\beta\tan^{-1}2\omega\tau)}{\omega\tau_{\text{c.o.}}(1+4\omega^2\tau_{\text{c.o.}}^2)^{\beta/2}}\Bigg]. \end{aligned} \tag{4}$$

Using (4) and the Arrhenius-type relationship between τ and the activation energy for the motion, we could reproduce the observed T_1 data below 200 K as shown in Fig. 3 by broken lines. The fitting of the T_1 values observed between 100 and 265 K, determined as the "melting point" of adsorbed water, was performed by applying (1) including the contributions from both mode **1** and mode **2**. The best-fitted curves and the determined values of parameters are shown by bold solid lines in Fig. 3 and Table 1, respectively.

Table 1. Motional constants (C), activation energies (E_a), and parameters representing the width of the τ distribution (β) obtained from T_1 curve fittings for tetramethylammonium (TMA) cations in saponite.

Specimen	$C \times 10^{-9}$ /s^{-2}	E_a /kJ mol^{-1}	β	Cationic motional mode
H_2O saturated	6.4	14 ± 2	0.22	CH_3-rot.
TMA-saponite	3.7	33 ± 2	0.28	isotropic rot.
anhydrous	1.4	7 ± 1	0.05	isotropic rot.
TMA-saponite	0.57	50 ± 3	0.25	self-diffusion

The calculation of motional constants C was carried out for two motions, *i.e.*, the methyl group rotation and the isotropic rotation of the whole cation using the "all staggered-conformation" of a TMA-cation. The obtained value 6.7×10^9 s^{-2} for mode **1** is close to 7.54×10^9 s^{-2} calculated for the methyl group rotation. Mode **2** is, accordingly, attributable to the isotropic rotation. Since the two minima overlap, the degree of τ distribution for mode **2** could not be accurately determined. By employing the calculated value of 3.7×10^9 s^{-2} for the isotropic rotation for the C value of mode **2**, we conducted the fitting and tentatively evaluated $\beta = 0.28$.

Two relaxation components were observed above 265 K near the melting point of surface water (cf. Figure 3). This indicates the presence of two kinds of cations in different motional states. Since the long T_1 was almost frequency independent and close to the theoretical curve for the isotropic rotation, it was assigned to the contribution from cations in the layer. On the other hand, the short T_1 with a Larmor frequency dependence and a rapid decrease upon heating can be assigned to the onset of a new motion of cations located near the layer edges or on the surface of clay. This motion is attributable to the cationic diffusion which is enabled by the melting of surface water.

Anhydrous TMA-Saponite

The observed two ^{1}H T_1 minima shown in Fig. 4 were explained by cationic motional processes named as mode **1** and **2** for the low and high temperature minima, respectively. The marked asymmetry observed in both minima implies the presence of a more serious τ distribution than in the hydrated specimen. This can be expected from the obtained T_1 values about 10 times longer than those in the D_2O saturated TMA-saponite [12]. We could reproduce the observed T_1 from two motional modes, both with a τ distribution

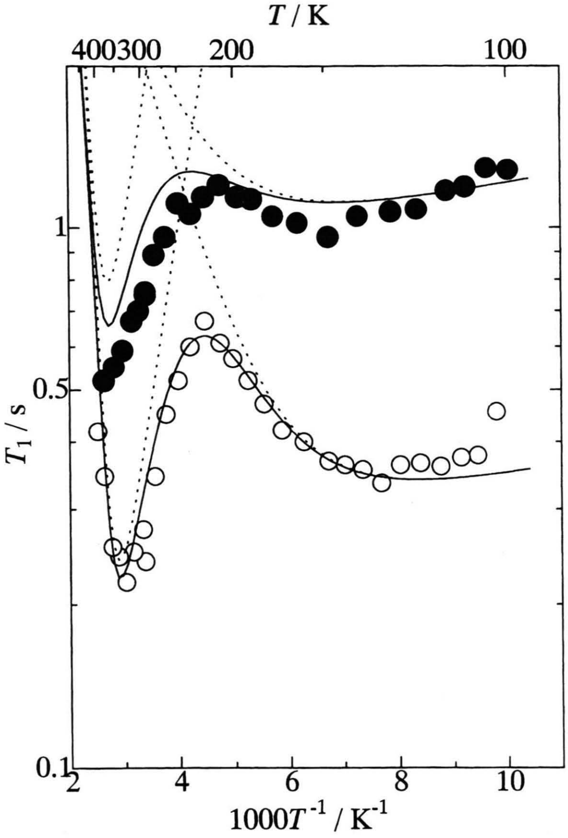

Fig. 4. Temperature and frequency dependences of ^{1}H NMR T_1 for anhydrous TMA-saponite observed at 14.9 (open circles) and 48.9 MHz (closed circles). Solid lines are the best-fitted curves assuming the Cole-Davidson type τ distribution.

given by (4) as shown in Figure 4. The fitted parameters are listed in Table 1. The C values obtained for mode **1** and **2**, 1.4×10^9 and 5.7×10^8 s^{-2}, respectively, were small compared to 7.54×10^9 s^{-2} calculated for the methyl rotation. Considering the facts that the ^{2}H NMR spectrum of anhydrous TMA-saponite showed the excitation of cationic isotropic rotation even at 120 K, and that a high activation energy of 50 ± 3 kJ mol^{-1} was obtained for mode **2**, the modes **1** and **2** seem to result from isotropic cationic rotation as a whole and translational self-diffusion, respectively.

The small value of $\beta = 0.1$ for mode **1** corresponds to a broad τ distribution originating from the marked inhomogeneity of the clay surface for the cationic rotation. The small activation energy of 7 ± 1 kJ mol^{-1}, evaluated for the isotropic rotation, implies that the cations are quite loosely bound in the interlayer space by weak electrostatic interaction. The barrier for rotation is higher in the water saturated saponite probably owing to the hindrance by surrounding water molecules.

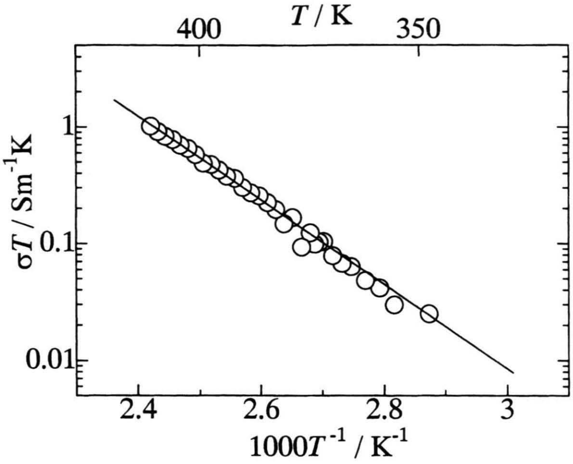

Fig. 5. Temperature dependence of the electrical conductivity $\sigma_{\parallel}$ measured at 1 kHz along the oriented clay plane using preferentially oriented films of anhydrous TMA-saponite. The solid line indicates a best-fitted line with the activation energy of 103 kJ mol^{-1}.

Electrical Conductivity

To confirm the cationic diffusion derived from the NMR T_1 analysis given above, we conducted measurements of the ac electrical conductivity σ on an oriented film of the anhydrous TMA-saponite. In this measurement, a marked anisotropy of the σ values was obtained, and $\sigma_{\perp}$, the value perpendicular to the layer, could not be determined in the whole temperature range studied because of its very high corresponding resistivity (larger than a few MΩ). On the other hand, $\sigma_{\parallel}$ parallel to the layer was high: 5×10^{-3} Sm^{-1} at 410 K. The temperature dependence of $\sigma_{\parallel}$ is shown in Figure 5. This result indicates that the ionic diffusion takes place along the clay-layer plane, supporting the above ^{1}H T_1 assignment. The activation energy of 103 ± 5 kJ mol^{-1} estimated for this diffusion is larger than that of 50 kJ mol^{-1} obtained from the NMR T_1 measurement. This disagreement is explainable by the differences in the diffusional motions measured by these two methods. Short range diffusion, such as jump to the nearest neighbouring sites contributes to the ^{1}H T_1, whereas the conductivity measured at 1 kHz is governed by long range diffusion over many lattice sites.

Conclusion

From measurements of the ^{1}H and ^{2}H NMR spectra in anhydrous and water saturated saponites, isotropic rotation of the TMA-cation was observed at temperatures above 120 K. We observed methyl rotation, isotropic rotation as a whole, and self-diffusion of TMA-cations by ^{1}H T_1 measurements. All of these motions showed a wide distribution of the motional correlation times, especially marked in anhydrous TMA-saponite. This can be attributed to the unequal crystal field at the cations arising from the inhomogeneous layer structure caused by the random distribution of Al in the saponite wall, and also irregular layer stackings in the specimen [9].

The ac electrical conductivity of anhydrous TMA-saponite showed a large anisotropy, the high value of 5×10^{-3} S m^{-1} having been observed in the direction along the clay layer.

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[1] G. Lagaly, Clay Miner. **16**, 1 (1981).

[2] G. Lagaly, Clays Clay Miner. **30**, 215 (1982).

[3] G. Sposit and R. Prost, Chem. Rev. **82**, 553 (1982).

[4] Chemistry of Clays and Clay Minerals, ed. by A. C. D. Newman, Mineral. Soc. of Great Britain Monograph No. 6, Wiley, New York 1987.

[5] B. Newmann, Rheolog. Acta **4**, 250 (1965).

[6] J. J. Fripiat, Advanced Chemical Method of Soil and Clay Minerals Research, ed. by J. W. Stucki and W. L. Banwart, D. Reidel Publishing Co., London 1980, pp. 245.

[7] P. Aranda and E. Ruiz-Hitzky, Chem. Mater. **4**, 1395 (1992).

[8] M. Ogawa and K. Kuroda, Chem. Rev. **95**, 399 (1995).

[9] X-ray Identification and Crystal Structure of Clay Minerals, ed. by G. Brown, Mineral. Soc. of Great Britain Monograph No. 5, Wiley, New York 1961.

[10] E. R. Andrew and P. C. Canepa, J. Magn. Reson. **7**, 429 (1972).

[11] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961.

[12] E. Göbel, W. Müller-Warmuth, and H. Olyschläger, J. Magn. Reson., **36**, 371 (1979).

[13] Progress of Intercalation Research in: W. Müller-Warmuth and R. Schöllhorn (eds.), Physics and Chemistry of Materials with Low-Dimensional Structures **17**, Kluwer Academic Pub., Dordrecht 1994.

[14] M. Molitor, Müller-Warmuth, H. W. Spieß, and R. Schöllhorn, Z. Naturforsch. **38a**, 237 (1983).

[15] S. Fukada, R. Ikeda, and D. Nakamura, Bull. Chem. Soc. Japan **57**, 2802 (1984).