

Chapter 4

Dynamics of Organocations Intercalated in Saponite

4.1 Results and Discussion

A. *n*-Octylammonium-Saponite (C81-SP and C81*d*₃-SP)

²H NMR spectra

²H NMR spectra observed in a temperature range 116-480 K are shown in Figure 4.A.1. These spectra consisted of superposed broad and sharp components. With increasing temperature, the broad component narrowed gradually and the proportion of the sharp one increased. This fact suggests that there are at least two kinds of ammonium groups in different motional states, namely, the sharp and broad components in the spectra originate from mobile and restricted ones, respectively. This phenomenon seems to come from the random distribution of anion centers in the clay sheets of saponite, because the motional state of positively charged ammonium groups must be sensitive to the anionic distribution. Thus, the wide component is assignable to ammonium groups near anion centers, the narrow one is to ammonium groups relatively apart from them. Quadrupole coupling constants (QCC) estimated from the linewidth of the broad component of ²H spectra are shown in Figure 4.A.2. The QCC of 50 ± 5 kHz obtained at 116 K was smaller than 58 kHz calculated for the rotating ND₃⁺ group about

its C_3 axis derived from 173 kHz observed in rigid $C_2H_5ND_3^+$ [8], indicating that this motional mode is already excited below 116 K. Moreover, the existence of the narrow component revealed that another motional mode averaging the quadrupole interaction more than the C_3 rotation is excited in some of *n*-octylammonium ions even at 116 K. Over a wide range 116-380 K, QCC gradually decreased from 50 to 16 ± 10 kHz being smaller than 22 kHz calculated for the model of the cationic uniaxial rotation about its long axis. This unusually gradual reduction implies that the reorientational correlation time of the uniaxial rotation is widely distributed. Since the linewidth of ca. 5 kHz was observed above 400 K, it is expected that a large amplitude motion of the whole ion in the two dimensional interlayer space is excited together with the axial rotation.

¹H NMR spectra

Figure 4.A.3 shows a temperature dependence of ¹H NMR spectra observed in C81-SP. All observed spectra seemed to be the superposition of two components with the approximately equal intensity. One component was sharp even at 108K and the other was narrowed with rising temperature. This fact suggests that there are two kinds of *n*-octylammonium ions in different motional states, in other words, two kinds of ions are placed in different circumstances. The broad component is assignable to intercalated ions which are motionally hindered in the interlayer space because magnetic dipole-dipole interactions are the origin of broadening. On the other hand, the sharp component is probably assigned to the ions located in the freely movable positions, such as the large room made between clay layers. This interpretation coincides with the result of

XRD and ^2H NMR spectrum analyses that interlayer distances in saponite compounds are much distributed and there are cations in the different motional states in the interlayer space of saponite.

Second moment of ^1H NMR spectra

Figure 4.A.4 shows the temperature dependence of second moment (M_2) of ^1H NMR spectra observed in C81-SP. The M_2 value at 107 K was $9 \pm 2 \text{ G}^2$. When the specimen was warmed from 107 to 200 K, M_2 decreased markedly from 9 to $4 \pm 1 \text{ G}^2$, and kept its value in 200-250K, then decreased slowly above 250 K. The theoretical M_2 values were calculated for the rigid lattice (M_2^{rigid}) of a *n*-octylammonium ion and for three possible motional modes (M_2^{rot}), the reorientation of the methyl group about the C_3 axis [CH₃-rot], the reorientation of the NH₃⁺ group about its C_3 axis together with the C_3 rotation of the CH₃ group, [CH₃-rot]+[NH₃⁺-rot], and the reorientation of the ion as a whole about its long axis in addition to the two motions mentioned above, by using the Van Vleck's formula expressed as [9]

$$M_2^{\text{rigid}} = \frac{6}{5} \gamma^2 \hbar^2 I(I+1) N^{-1} \sum_{k>l} r_{kl}^{-6} \quad (1),$$

$$\text{and} \quad M_2^{\text{rot}} = M_2^{\text{rigid}} \left(\frac{3 \cos^2 \alpha_{kl} - 1}{2} \right)^2 \quad (2),$$

where γ , I , N , r_{kl} , and α_{kl} are the gyromagnetic ratio of a proton, the proton spin quantum number, the number of protons in a cation, the length of dipolar vector between k th and l th protons, and the angle between a dipolar vector and its rotational axis, respectively. In the calculation, all bond angles in an ion were assumed to be tetrahedral and the C-H,

N-H, C-C and C-N bond distances were taken as 1.11, 1.05, 1.52 and 1.50 Å, respectively.

The M_2 of 9 G² observed at 107 K is smaller than 15 G² calculated for [CH₃-rot]+[NH₃⁺-rot]. This indicates that the rotations of both CH₃ and NH₃⁺ groups are excited below 100 K, and moreover the cationic uniaxial rotation is getting to be excited over the range 100-200 K, because the M_2 value finally reached 4 G² corresponding to 4.3 G² calculated for the onset of this mode. Although the QCC decreased quite gradually upon heating from 200 to 500 K, the corresponding M_2 reduction occurred relatively rapidly. This difference can be explained by considering that the QCC value was estimated selectively from the wide component of ²H spectra originating from the ions tightly fixed on the saponite sheet. On the other hand, since both broad and sharp components in ¹H spectra contribute to the M_2 , we obtained averaged M_2 values of both components.

¹H NMR spin-lattice relaxation time (T_1)

The ¹H NMR spin-lattice relaxation times (T_1) measured in C81-SP and C81d₃-SP are shown in Figure. 4.A.5. We observed a broad and a sharp minimum around 150 and 450 K, respectively. The T_1 data in C81-SP and C81d₃-SP were nearly the same in the whole temperature range studied except for the range 160-300 K, where T_1 in C8d₃-SP was longer than those in C81-SP. This T_1 behavior can be explained by assuming that the broad T_1 minimum consists of two minima: one in the high-temperature region, which was affected by the deuteration, is attributable to a motion associated with NH₃⁺

groups, while the other in low-temperatures can be explained by the CH₃ rotation. Taking into consideration of the QCC decrease in the range 116-480 K, The T_1 minimum observed around 450 K was assigned to the uniaxial rotation of n -octylammonium ions about the long axis. In case T_1 relaxation is caused by a molecular motion, the BPP-type equation with a single correlation time τ has been shown to be an acceptable approximation [10]. It is noted, however, that observed T_1 values around the minima are longer than those estimated from the simple BPP theory: the T_1 minimum values observed around 160 and 400 K were ca. 0.17 and 0.075 s, while those calculated for NH₃⁺ and uniaxial rotations are 0.13 and 0.021 s, respectively. To explain these shallow minimum values and, at the same time, the gradual reduction of QCC, we introduce a distribution in the correlation time τ . Assuming the Cole-Davidson type distribution [11] of τ given by

$$g(\tau) = \frac{\sin \beta \pi}{\pi} \left(\frac{\tau}{\tau_0 - \tau} \right)^\beta \quad \text{for } \tau \leq \tau_0$$

and $\quad = 0 \quad \quad \quad \text{for } \tau > \tau_0,$ (3)

where $\beta(0 < \beta \leq 1)$ is a measure of the distribution and τ_0 is the long limit of τ , T_1 can be written as

$$\frac{1}{T_1^{\text{DIS}}} = \frac{2}{3} \gamma^2 \Delta M_2 \left\{ \frac{\tau_0 \sin(\beta \tan^{-1} \omega \tau_0)}{\omega \tau_0 (1 + \omega^2 \tau_0^2)^{\beta/2}} + \frac{2\tau_0 \sin(\beta \tan^{-1} 2\omega \tau_0)}{\omega \tau_0 (1 + 4\omega^2 \tau_0^2)^{\beta/2}} \right\} \quad (4)$$

where γ , ΔM_2 , and ω are the gyromagnetic ratio of a proton, the reduction in M_2 of the ¹H NMR linewidth by the onset of the motion, and the angular Larmor frequency, respectively. Here, we assume an Arrhenius-type activation process given by

$$\tau_0 = \tau_\infty \exp \left[\frac{E_a}{RT} \right] \quad (5)$$

where E_a is the activation energy and τ_∞ is the cut-off correlation time in the limit of infinite temperature. The observed T_1 data in C81-SP were fitted by the superposition of three individual curves calculated by using Eqs. (3)-(5), as shown in Fig. 4.A.5, where dotted and broken lines are respective T_1 components calculated at 50.4 and 23.5 MHz and the superpositions are expressed by solid lines. The motional parameters determined by the fitting are shown in Table 4.A.1. It can be seen that T_1 calculated by introducing the τ distribution reproduces the experimental T_1 data, and ΔM_2 values obtained in this calculation agree well with those calculated for the CH_3^- , NH_3^+ - and uniaxial rotation as shown in Table 4.A.1.

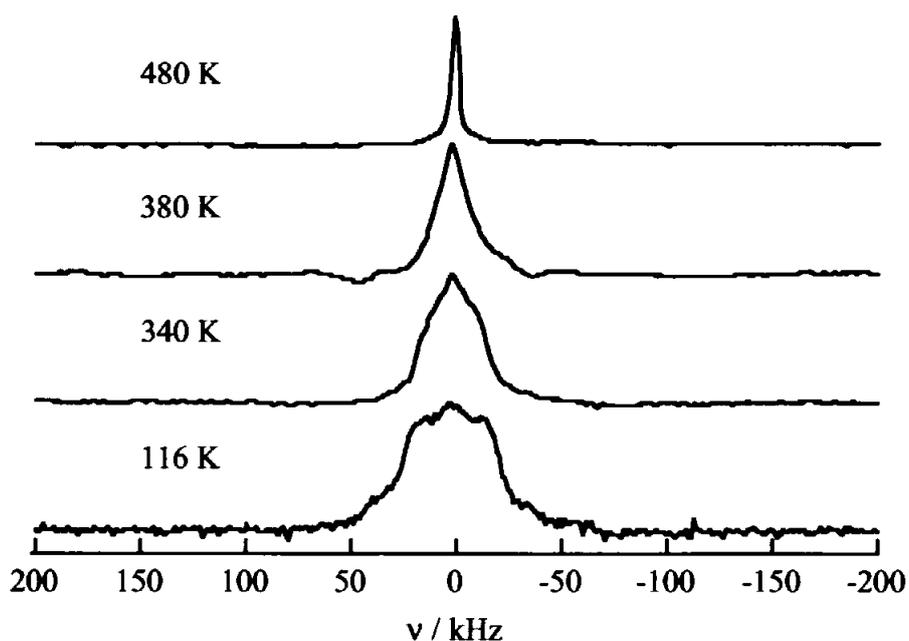


Fig. 4.A.1. ^2H NMR spectra observed in $\text{CH}_3(\text{CH}_2)_7\text{ND}_3$ -saponite.

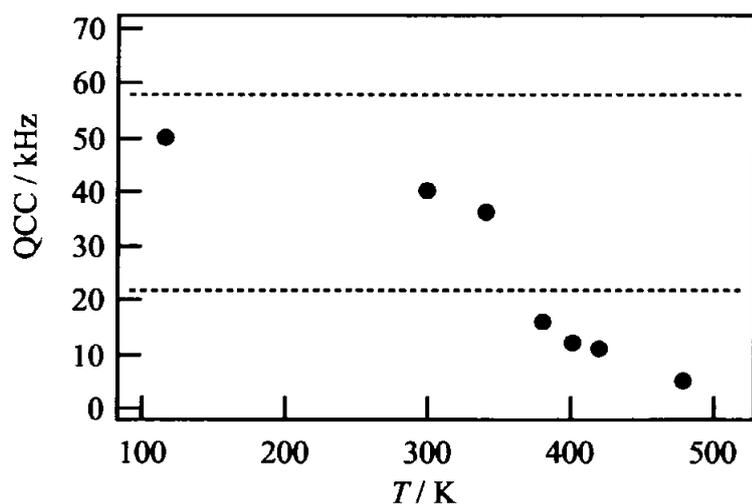


Fig. 4.A.2. The temperature dependence of quadrupole coupling constants (QCC) estimated from the linewidths of ^2H NMR spectra observed in $\text{CH}_3(\text{CH}_2)_7\text{ND}_3$ -SP. Broken lines stand for the calculated QCC for the motional modes of $\text{CH}_3(\text{CH}_2)_7\text{ND}_3^+$ ion: ND_3^+ group's rotation about its C_3 axis (upper) and the uniaxial rotation as a whole about its long axis (lower).

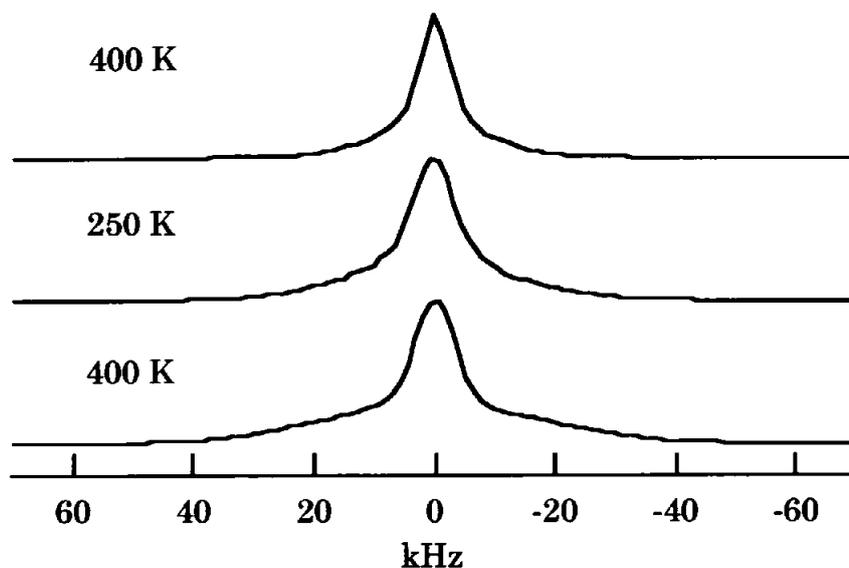


Fig. 4.A.3 ^1H NMR spectra observed in $\text{CH}_3(\text{CH}_2)_7\text{NH}_3$ -saponite.

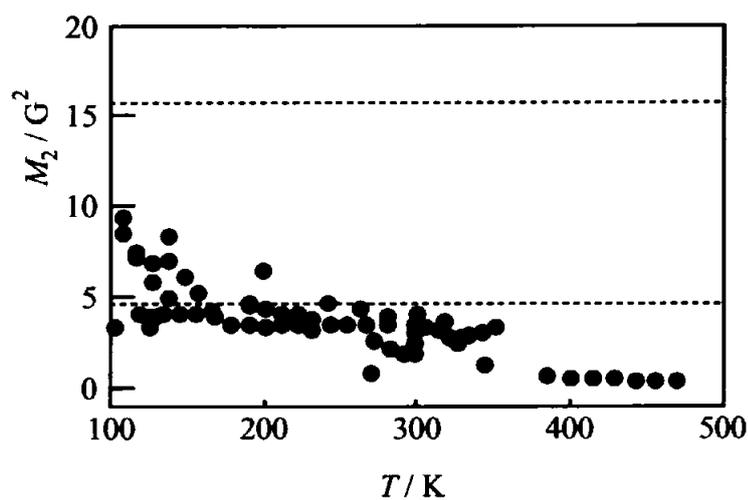


Fig. 4.A.4. ^1H NMR second moments (M_2) determined in $\text{CH}_3(\text{CH}_2)_7\text{NH}_3$ -saponite. Dotted lines denote M_2 values calculated for the onset of CH_3 and NH_3^+ rotations about their C_3 axes ($[\text{CH}_3\text{-rot}] + [\text{NH}_3\text{-rot}]$, upper) and the excitation of the cationic uniaxial rotation as a whole about its long axis together with $[\text{CH}_3\text{-rot}] + [\text{NH}_3\text{-rot}]$ (lower).

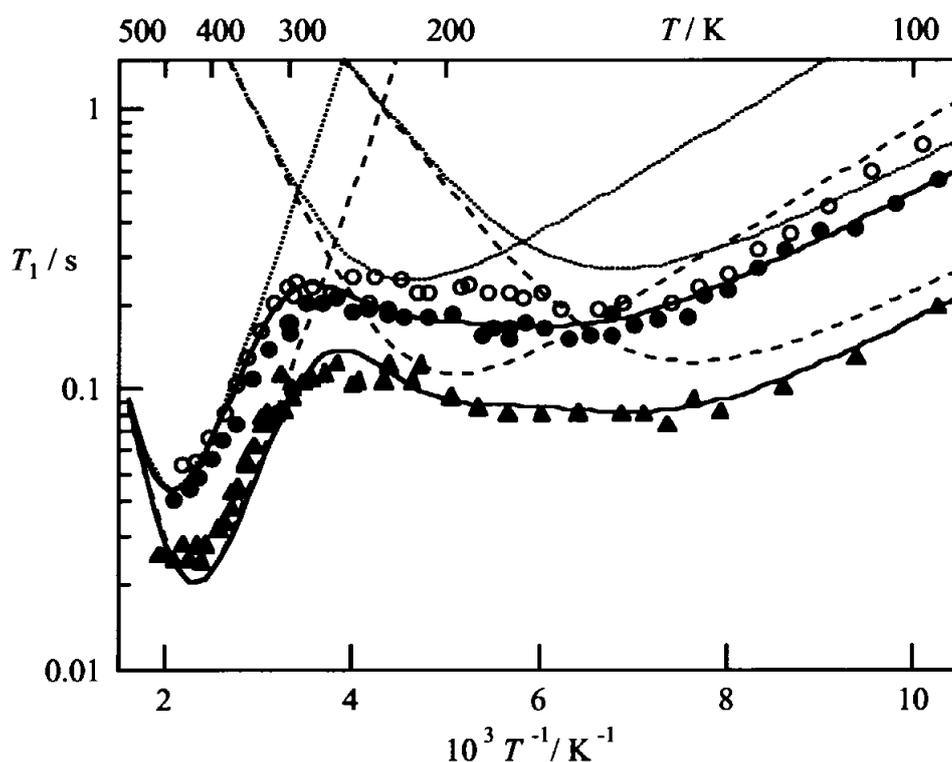


Fig. 4.A.5 ^1H NMR spin-lattice relaxation times T_1 observed at 50.4 MHz (●) and 23.5 MHz (▲) in $\text{CH}_3(\text{CH}_2)_7\text{NH}_3$ -saponite, and at 48.9 MHz (○) in $\text{CH}_3(\text{CH}_2)_7\text{ND}_3$ -saponite. Dotted and broken lines are respective T_1 components calculated at 50.4 and 23.5 MHz and the sums are expressed by solid lines.

Table 4.A.1. The fitting parameters of ^1H NMR spin-lattice relaxation times observed in $\text{CH}_3(\text{CH}_2)_7\text{NH}_3$ -saponite: motional modes, activation energies (E_a), reductions of second moment (ΔM_2) and parameters presenting width of τ distribution (β). Calculated values of ΔM_2 are shown in parentheses.

motional mode	$E_a / \text{kJ mol}^{-1}$	$\Delta M_2 / \text{G}^2$	β
CH_3 -rot	8.0	2.7(2.5)	0.4
NH_3^+ -rot	13	3.6(3.7)	0.3
uniaxial-rot	27	12(11)	0.7

B. *n*-Butylammonium-Saponite (C41-SP and C41*d*₃-SP)

²H NMR spectra

Figure 4.B.1 shows ²H NMR spectra observed in C41*d*₃-SP. With rising temperature, the spectrum linewidth narrowed gradually. Above 280 K, a sharp component like a bulge at the spectrum center, was growing up little by little with increasing temperature, and the only sharp component was observed at 470 K. These phenomena indicate that, in the temperature region above 280 K, there are at least two kinds of *n*-butylammonium ions, which are in different motional states. Quadrupole coupling constants (QCC) estimated from linewidths of the wide spectrum component are shown in Figure 4.B.2. Since QCC of 51 kHz obtained at 140 K is smaller than 58 kHz calculated for the ND₃⁺ rotation about its C₃ axis [ND₃⁺-rot], this mode can be regarded as already excited below 140 K. Over a wide temperature range from 140 to 430 K, QCC decreased gradually, and became about 25 kHz which is close to 22 kHz calculated for the cationic uniaxial rotation as a whole around the molecular long axis [uniaxial-rot]. This QCC behavior is similar to that observed in C8*d*₃-SP. As discussed in 4.1.A, it is provable that [uniaxial-rot] mode is gradually excited in this temperature region and this excitation is explained by the distributed correlation time. At temperatures above 450 K, QCC value became less than 22 kHz, indicating the onset of a new motional mode of *n*-butylammonium ion. Taking into consideration of the limited space between clay sheets, which is already confirmed by the XRD measurement at 500 K, a possible motional mode reducing QCC is the rotational reorientation of cations as a

whole about the axis perpendicular to the 2D plane.

¹H NMR spin-lattice relaxation time (T_1)

Figure 4.B.3 shows temperature dependences of ¹H NMR spin-lattice relaxation times observed in C41-SP and C41d₃-SP. Around 150 K, a T_1 minimum was observed in both C41-SP and C41d₃-SP. Upon heating from 300 K, T_1 was decreased steeply and a minimum appeared around 400 K at 25.6 MHz. By referring to the result of QCC in C41d₃-SP and T_1 analysis in C81-SP, T_1 curves in C41-SP could be reproduced by the superposition of three T_1 curves with distributed correlation times, which were already written in Eqs. (3)-(5), as shown in Figure 4.3.1. T_1 values observed in C41d₃-SP were longer than those in C41-SP in the temperature range from 150 to 300 K, implying that T_1 behavior in this region is governed by NH₃⁺ groups motion. Therefore, the T_1 minimum obtained by fitting calculation around 250 K is attributable to the C₃ rotation of NH₃⁺ groups, which is consistent with the result of ²H QCC in C41d₃-SP. From the analogy to T_1 analysis in C81-SP, the T_1 minima around 150 K and 400 K can be assigned to the C₃ rotation of CH₃ groups and the uniaxial rotation as a whole about the cationic long axis, respectively. The best fitted T_1 curves obtained in this T_1 analysis are shown in Figure 4.B.3. Dotted and broken lines stand for the calculated T_1 curves for each motional mode at 54.3 and 25.6 MHz, respectively, and superpositions of these contributions are drawn by solid lines. The motional parameters determined by the optimization are tabulated in Table. 4.B.1.

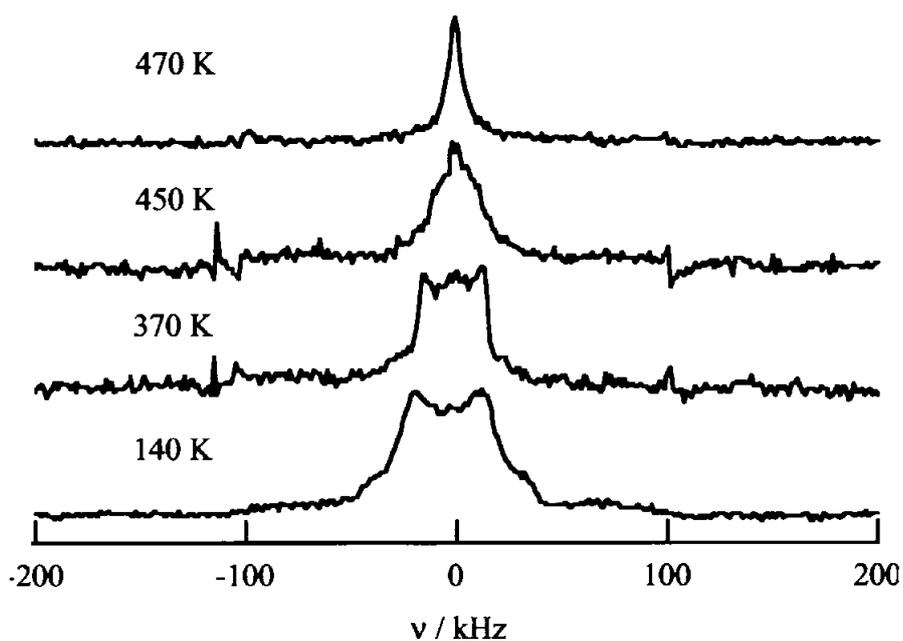


Fig. 4.B.1. ^2H NMR spectra observed in $\text{CH}_3(\text{CH}_2)_3\text{ND}_3$ -saponite.

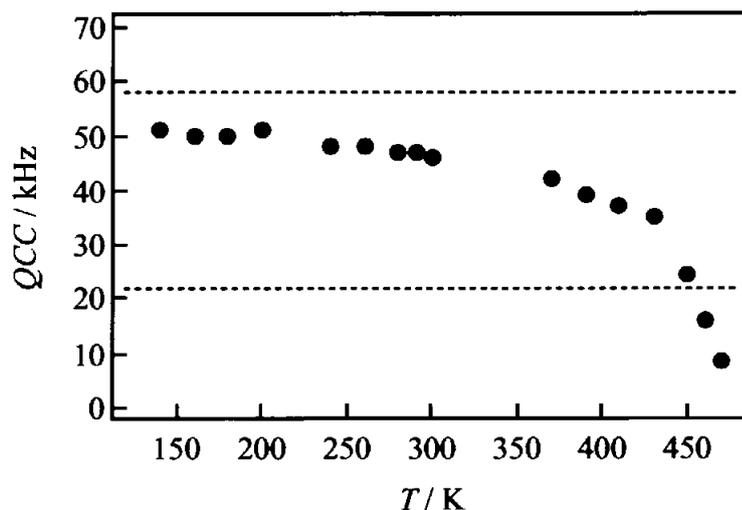


Fig. 4.B.2. The temperature dependence of quadrupole coupling constants (QCC) estimated from the linewidths of ^2H NMR spectra observed in $\text{CH}_3(\text{CH}_2)_3\text{ND}_3$ -saponite. Broken lines stand for the calculated QCC for the motional modes of $\text{CH}_3(\text{CH}_2)_3\text{ND}_3^+$ ion: ND_3^+ group's rotation about its C_3 axis (upper) and the uniaxial rotation as a whole about its long axis (lower).

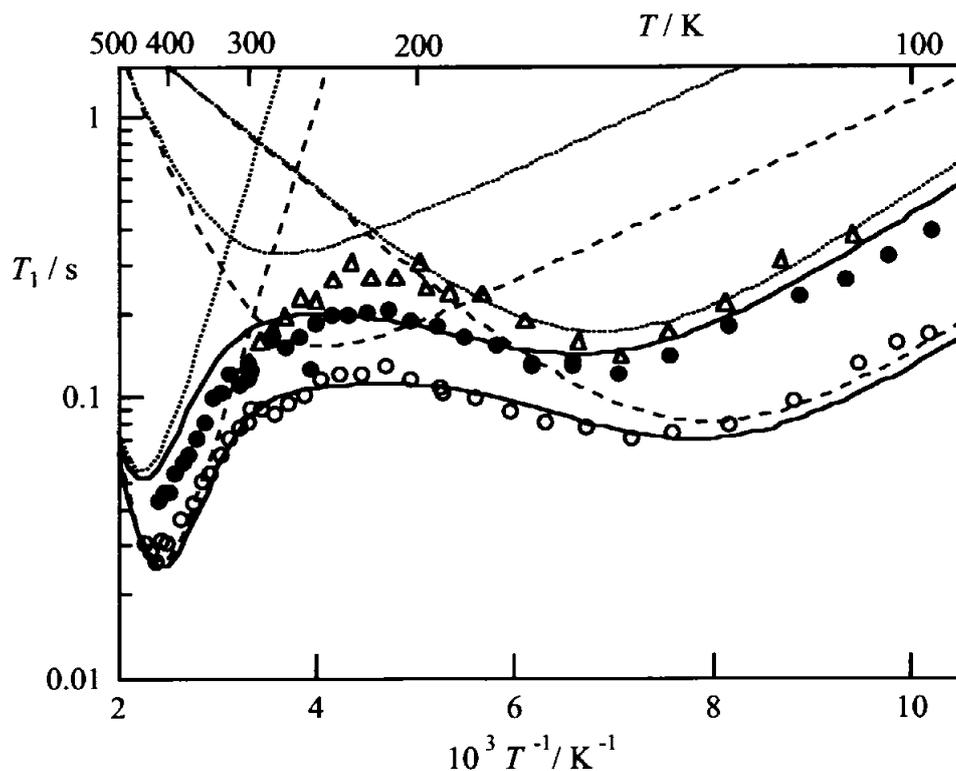


Fig. 4.B.3. ^1H NMR spin-lattice relaxation times T_1 observed at 54.3 MHz (●) and 25.6 MHz (○) in $\text{CH}_3(\text{CH}_2)_3\text{NH}_3$ -saponite, and at 54.3 MHz (△) in $\text{CH}_3(\text{CH}_2)_3\text{ND}_3$ -saponite. Dotted and broken lines are respective T_1 components calculated at 54.3 and 25.6 MHz and the sums of these contributions are expressed by solid lines.

Table 4.B.1. The fitting parameters of ^1H NMR spin-lattice relaxation times observed in $\text{CH}_3(\text{CH}_2)_3\text{NH}_3$ -saponite: motional modes, activation energies (E_a), reductions of second moment (ΔM_2) and parameters presenting the extent of distribution of correlation times (β).

motional mode	$E_a / \text{kJ mol}^{-1}$	$\Delta M_2 / \text{G}^2$	β
CH_3 -rot	5.7	3.9	0.8
NH_3^+ -rot	15	4.0	0.2
uniaxial-rot	33	13	0.7

C. Octamethylenediammonium-Saponite (C82-SP and C82d₆-SP)

²H NMR spectra

²H NMR spectra measured in C82d₆-SP are shown in Figure 4.C.1. The spectrum at 150 K was composed of two components whose linewidths were about 176 and 56 kHz, respectively. As shown in Fig. 4.C.1, the narrow component was major. With rise of temperature, the ratio of wide to narrow components decreased and the wide spectrum was faded above 350 K. With further increase of temperature, the linewidth of the main component was gradually reduced, a new sharp line appeared above 310 K, and, at last, only sharp line existed above 430 K. Quadrupole coupling constants (QCC) determined from linewidths of the major component are shown in Figure 4.C.2. The QCC of 56 kHz for the narrow component at 150 K is close to 58 kHz calculated for ND₃⁺ groups rotating around their C₃ axis [ND₃⁺-rot], indicating that this mode is already excited below 150 K. It was observed, however, that some of ND₃⁺ groups are in the rigid state even at 150 K because the minor component with a linewidth of 176 kHz corresponds to 173 kHz reported for rigid ND₃⁺ group in ethylammonium chloride [8]. Therefore, it is obvious that the circumstances of the ND₃⁺ groups in octamethylenediammonium ions are inhomogeneous in the interlayer space of saponite. Around 420 K, QCC jumped down to about 10 kHz being smaller than 22 kHz calculated for the uniaxial rotation of an octamethylenediammonium ion about its long axis. By referring to the previous discussion of C81d₃-SP, the gradual decrease of QCC over a wide temperature range from 280 to 420 K suggests the excitation of the uniaxial

rotation with a widely distributed correlation time. In the highest temperature region above 420 K, observed QCC of 10 kHz means the excitation of the rotational reorientation of cations as a whole about the axis perpendicular to the 2D plane (refer to 4.1.A and 4.1.B).

¹H NMR spin-lattice relaxation time (T_1)

Figure 4.C.3 shows temperature dependences of ¹H NMR spin-lattice relaxation times (T_1) observed in C82-SP and C82 d_6 -SP. From about 100 K, T_1 observed in C82-SP was decreased very slowly with the increase of temperature, and, between 180 and 300 K, no clear change was observed. A rapid reduction of T_1 was observed in the high temperature region above 300 K. Taking account of discussions in ²H spectra and their QCC analysis, it is acceptable to introduce the distributed correlation time in this T_1 analysis. T_1 curves in C82-SP were, accordingly, fitted by the superposition of three theoretical T_1 curves as given by Eqs. (3)-(5). Motional parameters determined in this optimization are shown in Table. 4.C.1. In the temperature range below 300 K, T_1 values obtained in C82 d_6 -SP are longer than those in the protonated compound, implying that the T_1 variation in C82-SP is appreciably connected to the motional state of NH₃⁺ groups because longer T_1 values in C82 d_6 -SP are explainable by less averaged dipolar interactions by motions of ND₃⁺ groups. Moreover, because the onset of [NH₃⁺-rot] below 150 K has already been confirmed by ²H spectrum analysis, two calculated minima are assignable to this mode. Generally, it is natural that the occurrence of one motional mode corresponds to observation of one T_1 minimum, but two minima were

given in this study. This phenomenon can be explained by quite large inhomogeneity in the circumstance of NH_3^+ terminal groups in C82-SP, that is, there are two extremes in NH_3^+ motional state: one is much freely movable, the other is motionally restricted. This consideration agrees with the ^2H NMR result showing two kinds of ND_3^+ groups in different motional states at 150 K. The T_1 reduction above 300 K can be attributed to the uniaxial rotation from analogy to the T_1 analysis in C81-SP.

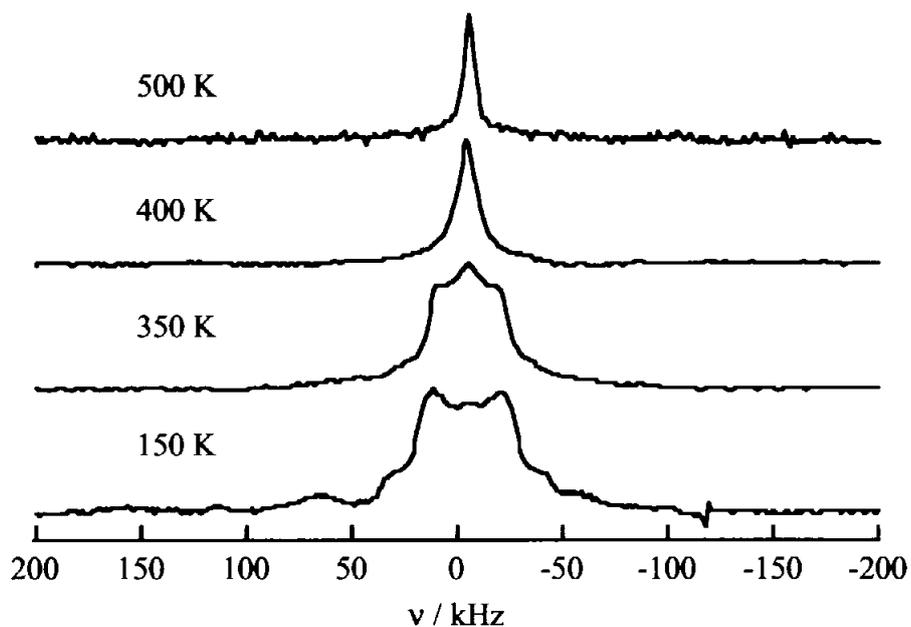


Fig. 4.C.1. ^2H NMR spectra observed in $\text{ND}_3(\text{CH}_2)_8\text{ND}_3$ -saponite.

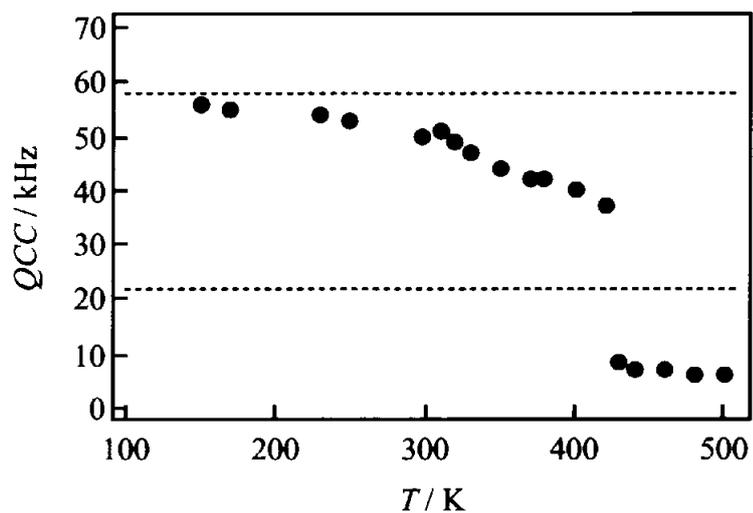


Fig. 4.C.2. The temperature dependence of quadrupole coupling constants (QCC) estimated from the linewidths of ^2H NMR spectra observed in $\text{ND}_3(\text{CH}_2)_8\text{ND}_3$ -SP. Broken lines stand for the calculated QCC for the motional modes of $\text{ND}_3^+(\text{CH}_2)_8\text{ND}_3^+$ ion: ND_3^+ group's rotation about its C_3 axis (upper) and the uniaxial rotation as a whole about its long axis (lower)

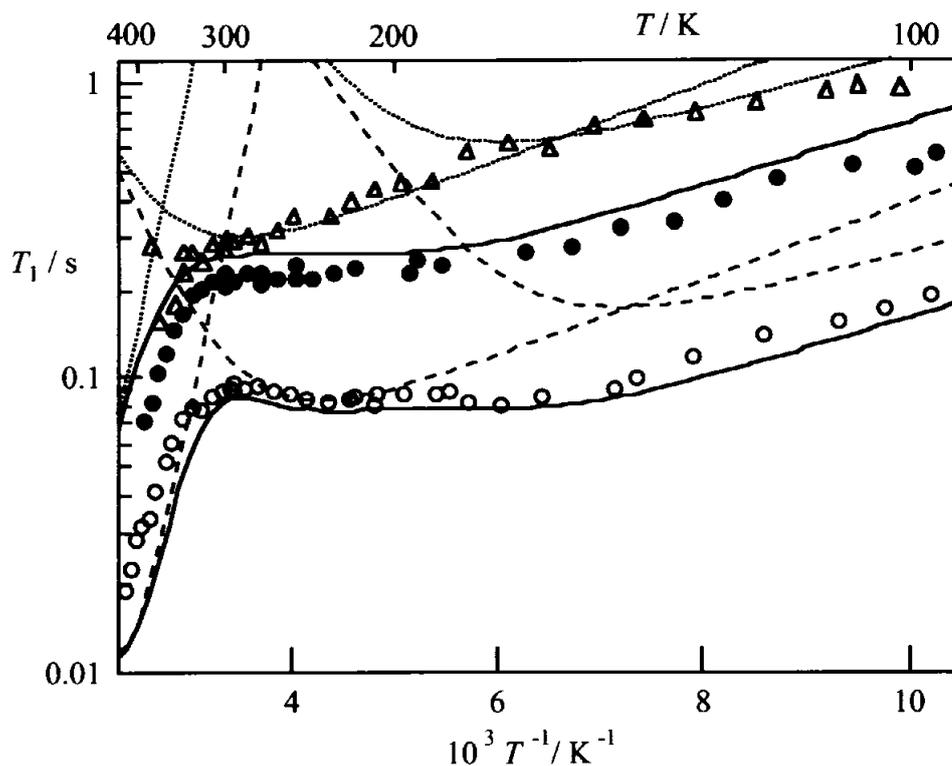


Fig. 4.C.3. ^1H NMR spin-lattice relaxation times T_1 observed at 54.3 MHz (●) and 15.0 MHz (○) in $\text{NH}_3(\text{CH}_2)_8\text{NH}_3$ -saponite, and at 54.3 MHz (△) in $\text{ND}_3(\text{CH}_2)_8\text{ND}_3$ -saponite. Dotted and broken lines are respective T_1 components calculated at 54.3 and 15.0 MHz and these superpositions are expressed by solid lines.

Table 4.C.1. The fitting parameters of ^1H NMR spin-lattice relaxation times observed in $\text{NH}_3(\text{CH}_2)_8\text{NH}_3$ -saponite: motional modes, activation energies (E_a), reductions of second moment (ΔM_2) and parameters presenting τ distribution width (β).

motional mode	$E_a / \text{kJ mol}^{-1}$	$\Delta M_2 / \text{G}^2$	β
NH_3^+ -rot	9.4	2.2	0.19
NH_3^+ -rot	14	4.7	0.18
uniaxial-rot	32	12	-

D. Tetramethylenediammonium-Saponite ($C_{42}d_6$ -SP and $C_{42}d_6$ -SP)

^2H NMR spectra

^2H NMR spectra observed in $C_{42}d_6$ -SP and quadrupole coupling constants estimated from their linewidths are shown in Figure 4.D.1 and 4.D.2, respectively. The temperature dependences of lineshapes and QCC values were almost same as those observed in $C_{82}d_6$ -SP, except for the fact that the wide spectrum component with a linewidth of about 180 kHz could not clearly be seen in Figure 4.D.1. Since QCC of 56 kHz observed at 140 K is close to 58 kHz of the calculated QCC for rotating ND_3^+ groups about their C_3 axes, it is expected that this mode is excited below 140 K. Between 200 and 360 K, the uniaxial rotation as a whole about the long axis is gradually occurred with the distributed correlation time in $C_{42}d_6$ -SP, because the gradual QCC reduction to 22 kHz, which is equal to that calculated for this mode, was observed in this temperature range. Although the explicit observation of the wide component could not be done at 140 K because of the poor signal intensity, it seemed that a wide component remains in the background of the spectra observed even at 350 K. So, it is very likely to be some distribution in the motional correlation time of tetramethylenediammonium ions in $C_{42}d_6$ -SP. In the high temperature region above 380 K, QCC values became much smaller than 22 kHz, implying the onset of a new motional mode, such as the rotational reorientation as a whole in the 2D space between clay sheets.

¹H NMR spin-lattice relaxation times (T_1)

Temperature dependences of ¹H NMR spin-lattice relaxation times observed in C42-SP and C42*d*₆-SP are shown in Figure 4.D.3. With increasing temperature, T_1 values observed in C42-SP was decreased very gradually in the temperature region of 100-300 K, and rapidly above 300 K. This phenomenon is also similar to that in C82-SP. From the QCC analysis in C42*d*₆-SP, it can be predicted that there is some distribution in the motional correlation time of tetramethylenediammonium ions, so T_1 curves in Fig. 4.D.3 were fitted by the superposition of three curves calculated by using Eqs. (3)-(5). In Fig. 4.D.3, dotted and broken lines are curves calculated at 54.3 and 15.0 MHz, respectively, and solid line is the superposition of curves calculated at each frequency. Fitting parameters in this optimization are shown in Table 4.D.1. T_1 values observed in C42*d*₆-SP were longer than those in C42-SP in all temperature range observed. From the analogy to the T_1 analyses in C82-SP and C82*d*₆-SP, it is provable to assign both two minima around 150 and 250 K to C_3 rotation of NH_3^+ groups of tetramethylenediammonium ions. T_1 reduction above 300 K in C42-SP is explainable by the onset of cationic uniaxial rotation as a whole because a corresponding QCC reduction was seen in C42*d*₆-SP.

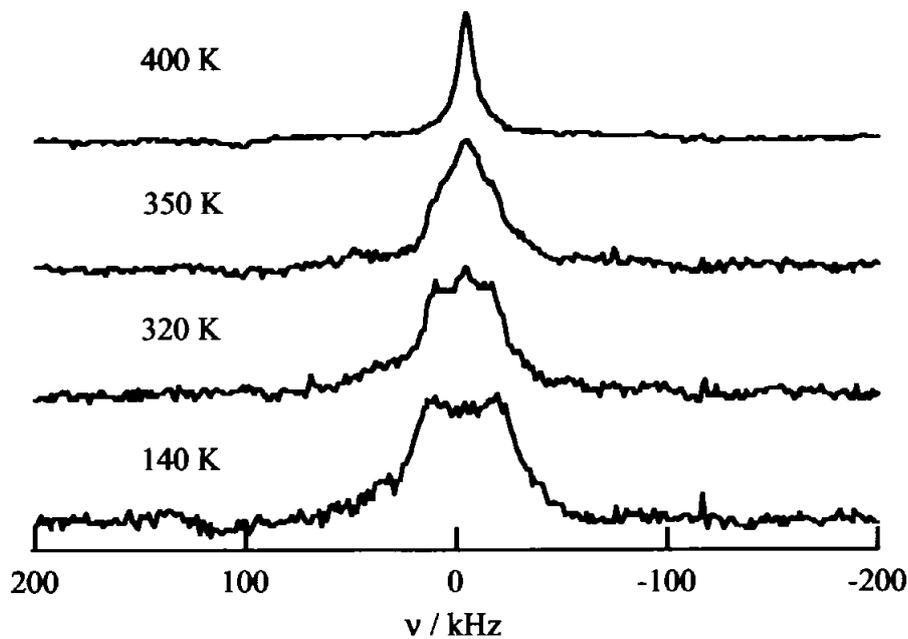


Fig. 4.D.1. ^2H NMR spectra observed in $\text{ND}_3(\text{CH}_2)_4\text{ND}_3$ -saponite.

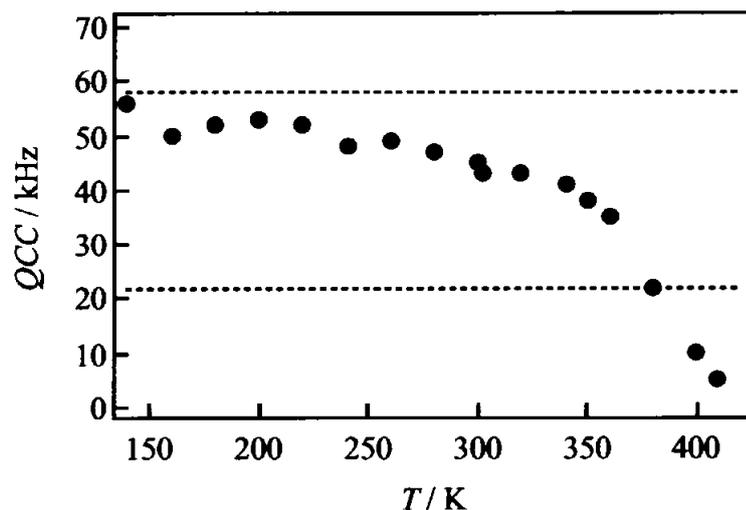


Fig. 4.D.2. The temperature dependence of quadrupole coupling constants (QCC) determined from the linewidths of ^2H NMR spectra observed in $\text{ND}_3(\text{CH}_2)_4\text{ND}_3$ -saponite. Broken lines stand for the calculated QCC values for the motional modes of $\text{ND}_3^+(\text{CH}_2)_4\text{ND}_3^+$ ion: ND_3^+ group's rotation about its C_3 axis (upper) and the uniaxial rotation as a whole about its long axis (lower).

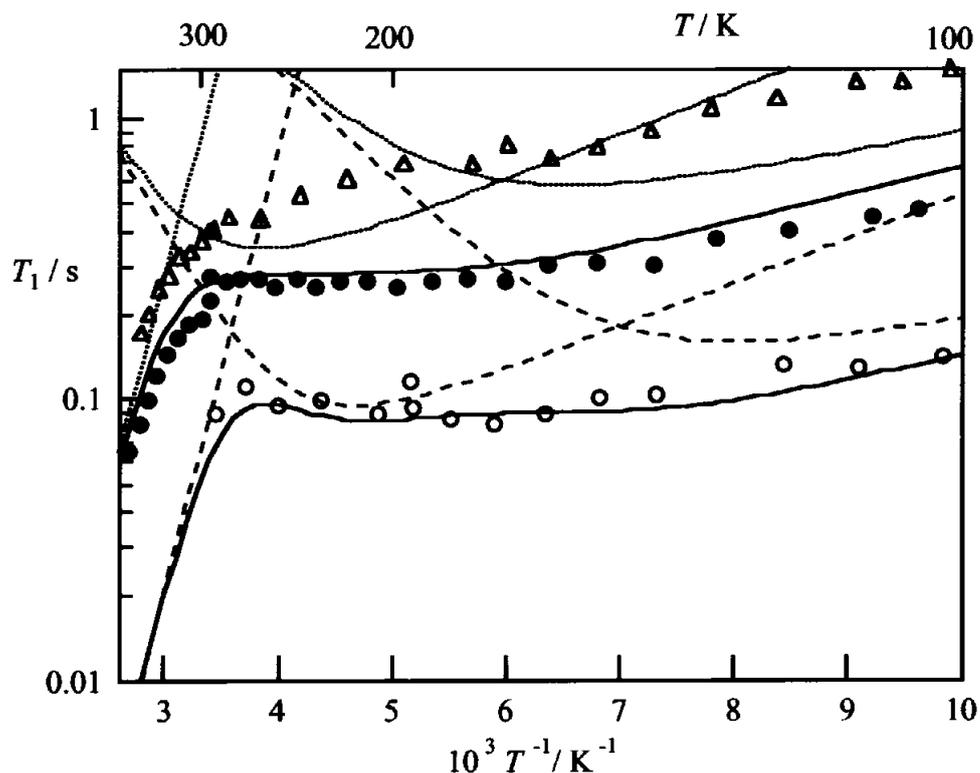


Fig. 4.D.3. ^1H NMR spin-lattice relaxation times T_1 observed at 54.3 MHz (\bullet) and 15.0 MHz (\circ) in $\text{NH}_3(\text{CH}_2)_4\text{NH}_3$ -saponite, and at 54.3 MHz (Δ) in $\text{ND}_3(\text{CH}_2)_4\text{ND}_3$ -saponite. Dotted and broken lines are respective T_1 components calculated at 54.3 and 15.0 MHz and these superpositions are expressed by solid lines.

Table 4.D.1. The fitting parameters of ^1H NMR spin-lattice relaxation times observed in $\text{NH}_3(\text{CH}_2)_4\text{NH}_3$ -saponite: motional modes, activation energies (E_a), reductions of second moment (ΔM_2) and a parameter presenting width of τ distribution (β).

motional mode	$E_a / \text{kJ mol}^{-1}$	$\Delta M_2 / \text{G}^2$	β
NH_3^+ -rot	7.4	2.3	0.20
NH_3^+ -rot	14	3.6	0.22
uniaxial-rot	30	-	-

E. Trimethylenediammonium-Saponite (C32-SP and C32 d_6 -SP)

²H NMR spectra

²H NMR spectra observed in C32 d_6 -SP are shown in Figure 4.E.1. At 140 K, a typical Pake pattern was obtained with a weak wide component which could be clearly seen in C82 d_6 -SP. Therefore, it is provable that the extent of distribution in the correlation time of NH₃⁺ groups motion in C32 d_6 -SP is smaller than that in C82 d_6 -SP. In the temperature region above 300 K, a new spectrum component appeared at the center, and the linewidth of the major component was narrowed to approximately 5 kHz at 500 K. Quadrupole coupling constants estimated from linewidths of spectra given in Fig. 4.E.1 are shown in Figure 4.E.2. Since a QCC value of 53 kHz determined at 140 K is smaller than 58 kHz calculated for the ND₃⁺ rotation about its C₃ axis, this mode is expected to be already excited below 140 K. A gradual QCC reduction could be seen between 140 and 400 K, and QCC of 15 kHz obtained at 400 K was smaller than 22 kHz calculated for the cationic uniaxial rotation as a whole about its long axis, indicating the onset of this rotation with a distributed correlation time. It is likely that the cationic in-plane reorientation as a whole occurs in the temperature region above 400 K since less than QCC of 10 kHz values were given, as is observed in other saponite compounds.

¹H NMR spin-lattice relaxation time (T_1)

The temperature dependence of ¹H NMR spin-lattice relaxation time observed in C32-SP is shown in Figure 4.E.3. With rising temperature, T_1 values decreased slowly, and a shallow T_1 minimum was found around 200 K, and above 300 K T_1 decreased rapidly. By referring to the QCC analysis in C32 d_6 -SP and results of the other saponite compounds, the T_1 curve in Fig. 4.E.3 was reproduced by the superposition of two T_1 curves calculated by using Eqs. (3)-(5). Dotted and solid lines depicted in Fig. 4.E.3 are calculated T_1 components and their superposition, respectively. Motional parameters given in this analysis are shown in Table. 4.E.1. As is distinct from C82-SP and C42-SP, T_1 data in the low temperature region below 300 K could be fitted by a single T_1 curve. This fact means that the circumstance around NH₃⁺ groups in a trimethylenediammonium ion is not so inhomogeneous compared with those in the other diammonium-saponite compounds. Taking into account of the QCC analysis in C32 d_6 -SP, the T_1 reduction above 300 K is attributed to the cationic uniaxial rotation as a whole about its long axis.

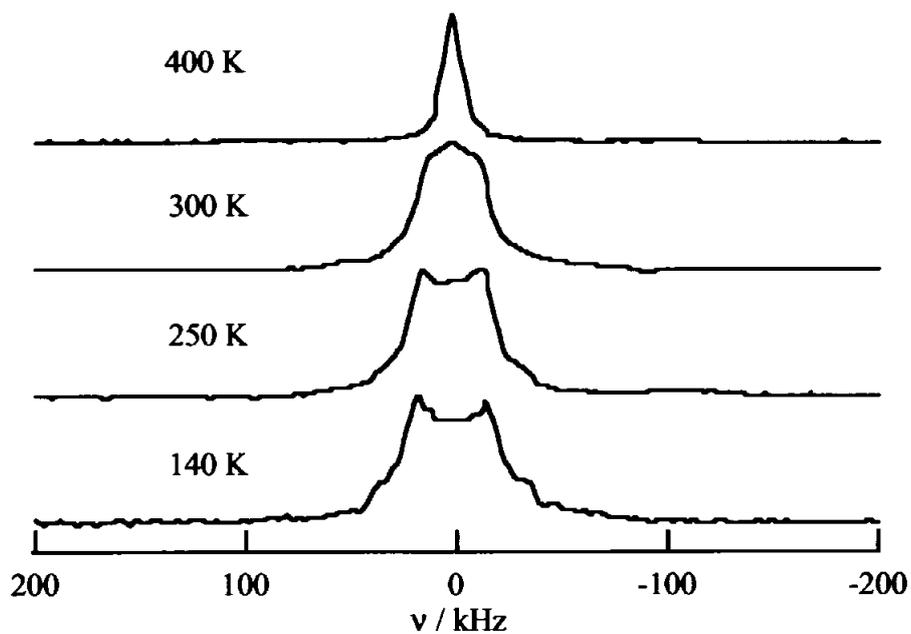


Fig. 4.E.1. ^2H NMR spectra observed in $\text{ND}_3(\text{CH}_2)_3\text{ND}_3$ -saponite.

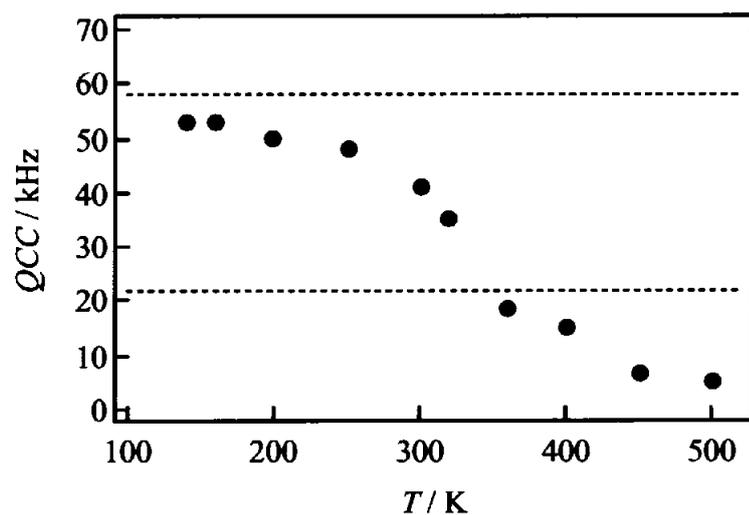


Fig. 4.E.2. The temperature dependence of quadrupole coupling constants (QCC) estimated from the linewidths of ^2H NMR spectra observed in $\text{ND}_3(\text{CH}_2)_3\text{ND}_3$ -saponite. Broken lines stand for the calculated QCC values for the motional modes of $\text{ND}_3^+(\text{CH}_2)_3\text{ND}_3^+$ ion: ND_3^+ group s rotation about its C_3 axis (upper) and the cationic uniaxial rotation as a whole about its long axis (lower).

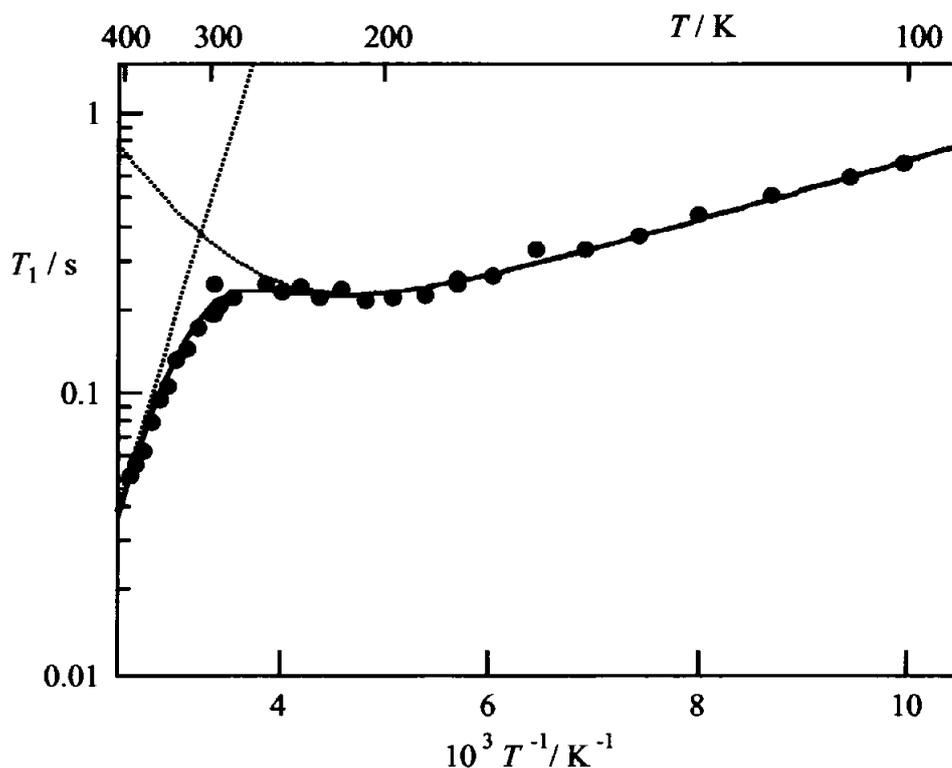


Fig. 4.E.3. ^1H NMR spin-lattice relaxation times T_1 observed at 54.3 MHz in $\text{NH}_3(\text{CH}_2)_3\text{NH}_3$ -saponite. Dotted lines denote T_1 values calculated at 54.3 MHz, and their superposition is expressed by a solid line.

Table 4.E.1. The fitting parameters of ^1H NMR spin-lattice relaxation times observed in $\text{NH}_3(\text{CH}_2)_3\text{NH}_3$ -saponite: motional modes, activation energies (E_a), a reduction of second moment (ΔM_2) and a parameter presenting width of τ distribution (β).

Motional amode	$E_a / \text{kJ mol}^{-1}$	$\Delta M_2 / \text{G}^2$	β
NH_3^+ -rot	9.3	5.5	0.22
uniaxial-rot	24	-	-

F. Guanidinium-Saponite ($\text{Gud}_6\text{-SP}$)

^2H NMR spectra

^2H NMR spectra observed in $\text{Gud}_6\text{-SP}$ are shown in Figure 4.F.1. The spectrum at 140 K had a very sharp component and a broad one with a complicate structure. The broad component seems to consist of two components: a broad one with line width of about 180 kHz and the other intermediate one with about 60 kHz. Therefore, it is expected that there are at least three kinds of ND_2 groups in different motional states in guanidinium ions between saponite layers. With rise of temperature, the intensity of the broadest component was reduced, but intermediate one increased. At 240 K, the broadest component could not be observed. In the high temperature region above 380 K, the intermediate component disappeared, and only sharp one remained. Quadrupole coupling constants (QCC) estimated from the line widths of broad and narrow spectral components are shown by open and close circles in Figure 4.F.2. In the temperature range 140-220 K, the QCC value determined from the broad component, was about 200 ± 20 kHz, which coincides with 200.5 kHz obtained in the rigid state of guanidinium chloride [12]. This fact means that some guanidinium ions are in the rigid state below 240 K. The ^2H QCC values in the rotating state of guanidinium ions (QCC_{rot}) is given by

$$\text{QCC}_{\text{rot}} = \text{QCC}_{\text{rigid}} * (1 - 3\cos^2\theta) / 2 \quad (6)$$

where $\text{QCC}_{\text{rigid}}$ is the QCC value of a guanidinium ion in the rigid state, and θ is the angle between a rotational axis and N-D bond axis. By using Eq. (6), the QCC value calculated for a rotating guanidinium ion as a whole about its C_3 axis is 100 kHz, which

agrees well with 100 ± 10 kHz estimated from a narrow component observed in the temperature range of 140-340 K. Therefore, it is probable that C_3 rotation is excited in some guanidinium ions. At 380 K, the QCC value jumped down to 27 kHz and decreased further to ca. 10 kHz with rising temperature to 440 K. Since such small QCC values are attained only by a quite large amplitude motion, it is expected that all of guanidinium ions in the isotropically rotational state in this high temperature region. It is remarkable that the sharp component, which is explainable by the onset of cationic isotropic rotation, exists even in the lowest temperature region together with broad and narrow ones. This indicates that there is a great extent of inhomogeneity in the circumstance surrounding guanidinium ions in saponite.

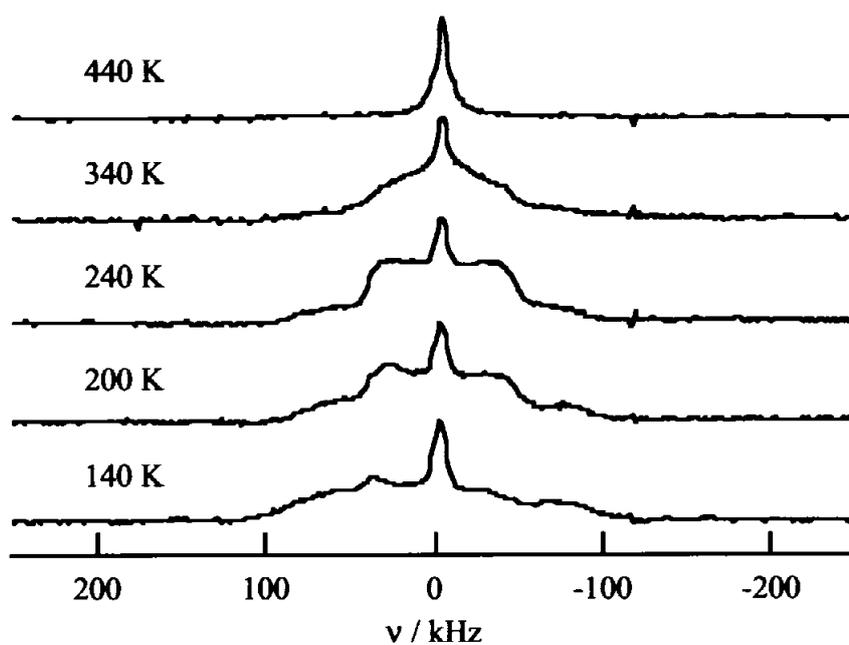


Fig. 4.F.1. ^2H NMR spectra observed in $\text{C}(\text{NH}_2)_3$ -saponite.

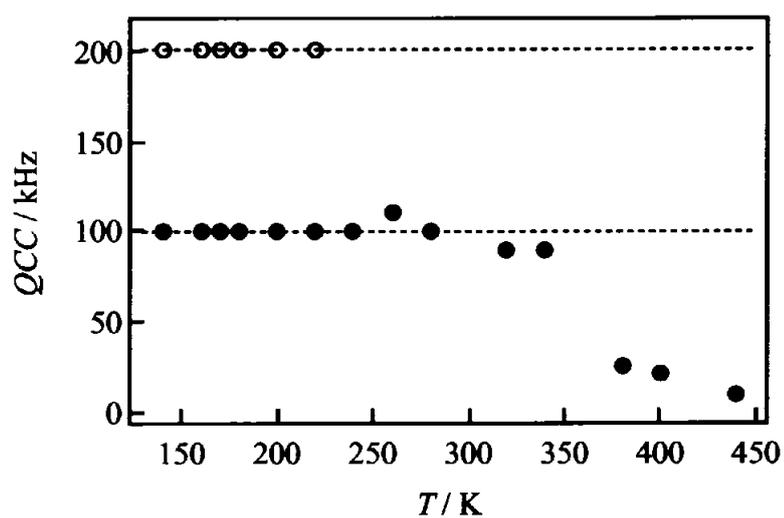


Fig. 4.F.2. The temperature dependence of quadrupole coupling constants (QCC) estimated from the linewidths of ^2H NMR spectra observed in $\text{C}(\text{ND}_2)_3$ -saponite. Broken lines stand for the calculated QCC for the motional modes of $[\text{C}(\text{ND}_2)_3]^+$ ions: rigid state (upper) and cationic rotation as a whole about its C_3 axis (lower).

4.2 Conclusion

A wide distribution in motional correlation times observed in n-alkylammonium-saponite series

The significant difference of dynamic properties of organocations in saponite intercalation compounds from those in bulk crystals is a wide distribution in their motional correlation times (τ). One of the reasons for the τ distribution is random dispersion of negative charges in saponite layers which brings in inhomogeneous environment around intercalated cations in the interlayer space of saponite.

A marked τ distribution can be seen in the NH_3^+ rotation of intercalated ions, as derived from small values of $\beta=0.2-0.3$ in Table 4.2.1. To explain this phenomenon, the following model in the interlayer spaces can be proposed: NH_3^+ groups of alkylmonoammonium ions in C81-SP and C41-SP tend to stay near the anion centers of the clay. But all cations cannot site the nearest position to anion centers because alkylmonoammonium ions are densely packed in C81-SP and relatively densely packed in C41-SP, with filling ratios of 77 and 50 %, respectively. In such a case, the activation barrier for NH_3^+ rotation depends on the cationic position, because the motion of the positively charged NH_3^+ groups is governed by the electrostatic attraction with the clay wall. Hence, the motional correlation time in NH_3^+ rotations is distributed in the interlayer space of saponite.

It is found that two kinds of activation energies were obtained for the NH_3^+ rotation in C82-SP and C42-SP while a single value in C81-SP, C41-SP and C32-SP.

As for alkyldiammonium ions in C82-SP and C41-SP, because of the presence of two NH_3^+ groups in an ion and the packing of these cations in the limited interlayer space, it seems to be difficult that both terminal NH_3^+ groups stay at the same distance from anion centers in the clay sheets. Hence, the circumstances of NH_3^+ groups are different at both terminals, and two kinds of activation energies for NH_3^+ rotations are likely obtained in C82-SP and C42-SP. In contrast, the case in C32-SP can be explained by only a single activation energy for the NH_3^+ rotation. Because trimethylenediammonium ions exist apart from each other in the interlayer space with a filling ratio of 29 %, they can easily take their favorable arrangements in the interlayer space. Moreover, it is also possible that both terminal NH_3^+ groups of trimethylenediammonium ions stay near the anion center simultaneously, since the distance between terminals is relatively short. Accordingly, a single activation energy for the NH_3^+ rotation is provably given in both NH_3^+ groups of trimethylenediammonium ions.

Finally, it can be concluded that dynamic properties of NH_3^+ groups is governed by the charge distribution of saponite layers and the structures of cations in the interlayer spaces.

Influence of inhomogeneity of interlayer distances in saponite

If saponite layers closely sandwich the intercalated cations, the activation energy for the cationic uniaxial rotation as a whole, [uniaxial-rot], should be different with the ionic size (length). Observed activation energies for this mode, however, are almost same in the alkylammonium-saponite series. Therefore, it is likely that this result

originates from the inhomogeneity of interlayer distances of saponite compounds, that is, much inhomogeneity of the interlayer distance compensates the effect of the molecular size to the motional states of intercalated ions in saponite.

Difference in dynamic properties of organocations in saponite intercalation compounds from those in bulk crystals

It is noteworthy that activation energies for the uniaxial rotation in intercalated ions are higher than those in pure crystalline alkylammonium halides. For example, E_a values for this mode in saponite compounds are 24-27 kJ mol⁻¹. On the other hand, 5-18 kJ mol⁻¹ have been reported in alkylammonium halides [12-14]. The interlayer distances of the saponite compounds other than Gu-SP are estimated to be ca. 4 Å, smaller than ca. 5 Å of the distance between the nearest alkylammonium ions in the pure crystals[12, 14]. Therefore, it can be said that high E_a values for the uniaxial rotation in saponite compounds are attributed to the spatial limitation from the small interlayer space sandwiched by clay sheets.

Table 4.2.1 Motional parameters determined in saponite compounds in this study by ^1H NMR measurements: motional modes, activation energies (E_a), and parameters presenting width of τ distribution (β).

compound	motional mode	$E_a / \text{kJ mol}^{-1}$	β
C81-SP	CH_3 -rot	8.0	0.40
	NH_3^+ -rot	13	0.30
	uniaxial-rot	27	0.70
C41-SP	CH_3 -rot	5.7	0.80
	NH_3^+ -rot	15	0.20
	uniaxial-rot	33	0.70
C82-SP	NH_3^+ -rot	9.4	0.19
		14	0.18
	uniaxial-rot	32	-
C42-SP	NH_3^+ -rot	7.4	0.20
		14	0.22
	uniaxial-rot	30	-
C32-SP	NH_3^+ -rot	9.3	0.22
	uniaxial-rot	24	-