Dynamics of Two-Dimensionally Arranged *n*-Octylammonium Ions Intercalated into Tetrasilicicfluormica

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The dynamic behaviour of *n*-octylammonium ions intercalated into tetrasilicicfluormica was investigated by measuring ^{1}H and ^{2}H solid state NMR spectra and ^{1}H spin-lattice relaxation times. X-Ray diffraction measurements revealed that the cations are arranged with the long axis parallel to the clay sheet. Uniaxial rotation of cations was found to take place above ca. 200 K among non-equivalent potential wells made by clay sheets. As a new type of 2-D motion mode, whole cationic in-plane tumbling in the 2-D layer seems to be excited above ca. 450 K. The obtained results are compared with those previously reported on saponite of an analogous structure.

Key words: Tetrasilicicfluormica; *n*-Octylammonium Ion; ^{1}H and ^{2}H NMR; Intercalation Compound; Spin-Lattice Relaxation.

Introduction

It is a characteristic of layered clay minerals that a two-dimensionally (2-D) extended space is formed between the layers in which many kinds of chemical species can be intercalated. Alkylammonium ions, e.g., have been reported to form a characteristic layer structure depending on their length and the cation exchange capacity (CEC) of clays [1]. In clays with large CEC, e.g. vermiculite, densely packed alkylammonium ions form mono- or bilayers. With increase of the carbon number in the alkyl groups, the basal spacing between layers is expanded by a constant increment per carbon atom, indicating that long chains are inclined 50–60° to the clay sheet [2]. On the other hand, in smectites with small CEC values, alkylammonium ions are arranged with their long axes parallel to the clay layer, forming mono- to trilayers according to their chain lengths [3]. We are interested in the dynamic properties of intercalated ions in this type of clays because guest ions in the 2-D space are expected to exhibit unique properties of 2-D ionic systems as to molecular motions, phase transitions and ionic conductivity.

Tetrasilicicfluormica ($A^{n+}_{1/n}Mg_{2.5}Si_4O_{10}F_2$), a layered clay, forms layers of 2-D connected MgO_4F_2 octahedra sandwiched between two layers consisting of vertex sharing SiO_4 tetrahedra. The presence of vacancies at one-sixth of the magnesium sites implies negative charge generation in the mica layers, which requires compensating positive ions in the space between the layers. Since this clay can be synthesised without contamination by paramagnetic species causing strong paramagnetic effects to surrounding atoms, it is suitable for the NMR measurement. In [4] we reported a 2-D structure and the dynamics of *n*-octylammonium ions intercalated in saponite, in which large-amplitude cationic motions take place in the 2-D space with a marked distribution of the motional correlation time originating from widely spread charge distributions in the clay wall. Tetrasilicicfluormica, in which the charge distribution is expected to be smaller and the crystalline sizes are much larger than those in saponite, is a suitable clay to investigate the molecular dynamics of guest molecules in a 2-D structure.

In the present study we have investigated the dynamic properties of intercalated ions in *n*-octylammonium-tetrasilicicfluormica by measuring ^{1}H and ^{2}H solid state NMR and X-ray powder diffraction.

Experimental

Synthetic sodium-tetrasilicicfluormica ($Na_{2x}Mg_{(3-x)}Si_4O_{10}F_2, x = 0.3$), abbreviated Na-MC, with a cation exchange capacity (CEC) of 70–80 meq/100 g was obtained from CO-OP Chemical Co., Ltd. The intercalation of *n*-octylammonium ions into the clay was performed by the conventional ion exchange method using an aqueous solution of *n*-octylammonium chloride with a concentration adjusted to twice the CEC of the Na-MC. After the exchange, the product was filtered and washed with distilled water repeatedly until the negative $AgNO_3$ test was obtained.

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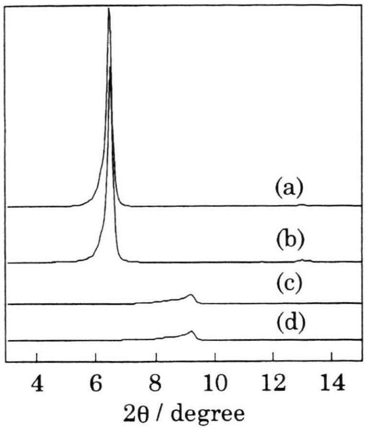

Fig. 1. X-Ray powder diffraction patterns observed in n-$C_8H_{17}NH_3$-mica at 400 (a) and 300 K (b), and Na-mica at 400 (c) and 300 K (d).

Deuteration of NH_3^+ groups in *n*-octylammonium ions in C8-MC was carried out by keeping an intercalated specimen in a saturated vapour of 99.5% heavy water at room temperature for two days. Deuterated C8-MC is abbreviated to C8d_3-MC.

X-Ray powder diffraction patterns were measured in Na-MC and C8-MC with a PHILIPS X'pert PW 3040/00 diffractometer using Cu(Kα) radiation. The data were collected between 1 and 30 ° at 300 and 400 K.

^{1}H and ^{2}H NMR spectra were observed at Larmor frequencies of 300.13 and 46.05 MHz, respectively, in both C8-MC and C8d_3-MC with a Bruker MSL-300 NMR system at 100–500 K.

Temperature dependences of the ^{1}H NMR spin-lattice relaxation time (T_1) were measured for C8-MC and C8d_3-MC with a home-made apparatus using the 180°-τ-90° pulse sequence at 100–410 K. Larmor frequencies of 48.9 and 25.6 MHz were employed for C8-MC and of 48.9 MHz for C8d_3-MC.

Results and Discussion

Elemental Analysis and X-Ray Diffraction

From the elemental analysis of C8-MC, ca. 60% of Na^+ ions in Na-MC were shown to be exchanged by *n*-octylammonium cations, i.e., one alkylammonium cation is intercalated per approximately eight Si atoms forming four silicate rings in clay layers.

X-Ray powder patterns of Na-MC and C8-MC observed at 300 ± 1 and 400 ± 2 K, respectively, are shown in Figure 1. Interlayer distances in these compounds were obtained by subtracting the layer thickness of 0.96 nm [5] from observed *d*-spacings derived from (001) reflections, and are listed in Table 1. It is obvious that the interlayer spacing in C8-MC is expanded by ca. 0.4 nm, indicating that alkylammonium ions are intercalated into the interlayer space with the long axis parallel to the layer. This is because this expansion corresponds to the short diameter of ca. 0.42 nm of an *n*-octylammonium ion with the trans zigzag conformation. It is noted from the X-ray diffraction that the interlayer distance is almost independent of temperature in a range 300–400 K. This suggests that alkylammonium motions requiring a large excess space perpendicular to the clay layer, such as the overall rotation of the alkyl-chain with conformational changes, are restricted even at 400 K.

Table 1. $d(001)$ spacings in Na-mica (Na-MC) and n-$C_8H_{17}NH_3$-mica (C8-MC) derived from X-ray powder diffraction data obtained at 300 and 400 K. Interlayer distance calculated by subtracting the layer thickness 0.96 nm from respective $d(001)$ spacings are shown in parentheses.

	$d(001)$/nm	
T/K	Na-MC/nm	C8-MC/nm
300	0.96 ± 0.1 (~0.0)	1.40 ± 0.05 (0.44)
400	0.96 ± 0.1 (~0.0)	1.38 ± 0.05 (0.42)

^{1}H NMR Spectra

A temperature dependence of ^{1}H NMR spectra observed in C8-MC is shown in Figure 2. All spectra could be explained by the superposition of two components consisting of a major broad and a minor sharp signal. The latter component could be observed even at 108 K, while the former was narrowed upon heating. These facts imply the existence of two kinds of *n*-octylammonium ions in different motional states, or in different circumstances. It has been reported that small amounts of the alkylammonium ions are bounded to crystal edges of smectites having similar structures to that of mica [3]. The sharp component is, accordingly, assignable to movable ions located in spatially less-restricted positions, such as crystal edges. On the other hand, the broad component is due to intercalated *n*-octylammonium ions because motions of these ions are expected to be much restricted and cannot fully average the magnetic dipolar interactions.

^{2}H NMR Spectra

The temperature dependence of ^{2}H NMR spectra in C8d_3-MC observed at 108–480 K is shown in Figure 3. The spectrum at 108 K exhibits a typical Pake pattern

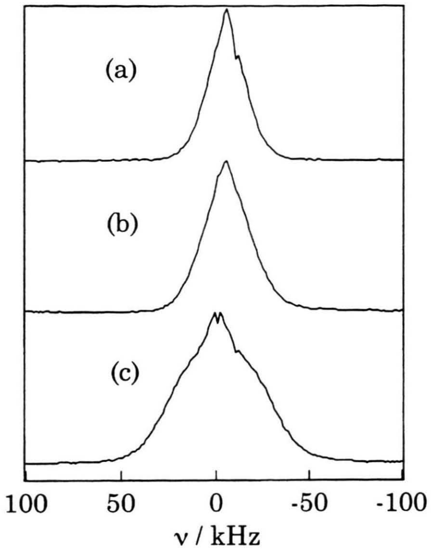

Fig. 2. ^{1}H NMR spectra observed in *n*-$C_8H_{17}NH_3$-mica at 390 (a), 295 (b) and 116 K (c).

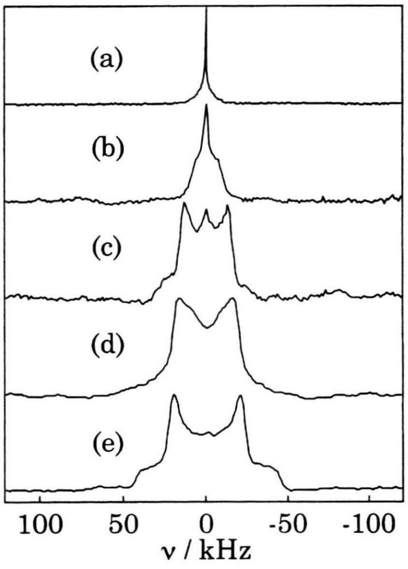

Fig. 3. ^{2}H NMR spectra in *n*-$C_8H_{17}ND_3$-mica at 480 (a), 460 (b), 430 (c), 300 (d), and 108 K (e).

with a small asymmetry parameter, $\eta \leqq 0.1$. A spectrum narrowing was observed with increasing temperature and, above 400 K, another spectral component appeared at the centre. In consistence with the ^{1}H NMR spectrum analysis, the major broad component can be assigned to octylammonium ions in the interlayer space, while the sharp one is attributable to ions on crystal edges.

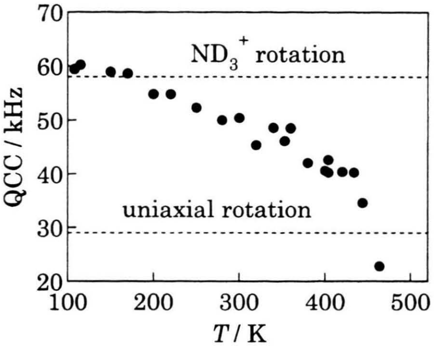

Fig. 4. The temperature dependence of the ^{2}H quadrupole coupling constant (QCC) in *n*-$C_8H_{17}ND_3$-mica. Broken lines stand for calculated values for the NH_3^+ and uniaxial reorientations.

The quadrupole coupling constants (QCC) of the broad component were estimated from the width between two peaks by assuming $\eta = 0$. Its temperature dependence is shown in Figure 4. Calculations of theoretical QCC's were carried out for possible motional modes in the interlayer space, i.e., reorientation of the ND_3^+ group about its C_3-axis [ND_3^+-rot], and the cationic uniaxial rotation as a whole about its long axis [(ND_3^++chain)-rot]. In this calculation we employed the QCC of 173 kHz reported for rigid $C_2H_5ND_3Cl$ at 77 K [6], and assumed tetrahedral bond angles in the cation. The calculated values of 58 and 29 kHz for [ND_3^+-rot] and [(ND_3^++chain)-rot], respectively, are shown in Fig. 4 by broken lines. Onset of the ND_3^+ reorientation is expected below 108 K because the observed QCC of 60 ± 2 kHz is explainable by this motion.

A gradual reduction of QCC to 34 ± 2 kHz, observed in the wide temperature range of 150 – 440 K, can be explained by the excitation of the uniaxial reorientation of *n*-octylammonium ions by referring to 29 kHz calculated for this motion. This unusual gradual QCC reduction is attributable to motion taking place between asymmetric potential wells, because two unequal wells for parallel and perpendicular orientations of the trans-zigzag plane to the clay sheets are plausible. Since the long and short diameters of an *n*-octylammonium ion are estimated to be ca. 0.45 and 0.42 nm, respectively, two different orientations of a cation in the asymmetric potential wells can be obtained as illustrated in Figure 5.

Above 460 K, the line-width of the outer component in the ^{2}H NMR spectra was narrowed to less than 3 kHz. This indicates the excitation of another motion such as whole ionic rotation around the axis perpendicular to the molecular axis because only this mode can reduce the line-width to the observed value with negligible expan-

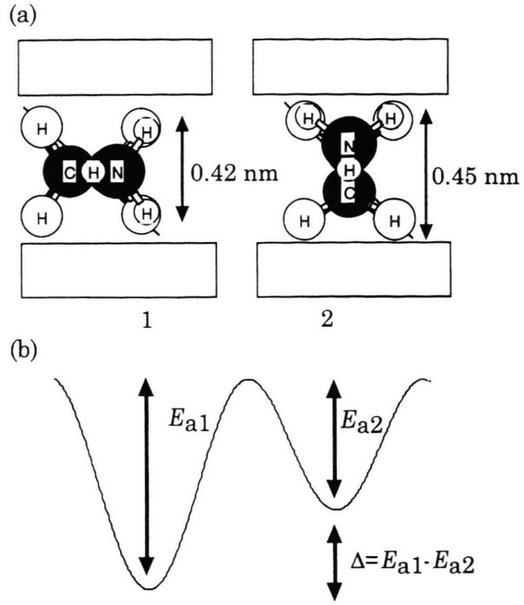

Fig. 5. (a) Two non-equivalent orientations (1 and 2) of an n-$C_8H_{17}NH_3^+$ ion in the interlayer space. (b) The asymmetric potential model for two non-equivalent orientations with activation energies of E_{a1} and E_{a2} for the n-$C_8H_{17}NH_3^+$ reorientation.

sion of the interlayer space. The same kind of ^{2}H spectrum narrowing at high temperatures assignable to this whole cationic motion was observed in the *n*-octylammonium saponite system already reported [4].

^{1}H NMR Spin-Lattice Relaxation Times (T_1)

^{1}H NMR T_1 values measured in C8-MC at 48.9 and 25.6 MHz, and C8d_3-MC at 48.9 MHz are plotted in Figure 6. A frequency dependent T_1 was observed in C8-MC at 89–400 K, indicating the presence of magnetic dipolar relaxation processes. T_1 in C8-MC observed at 48.9 MHz showed a broad and a sharp minimum at ca. 130 and 300 K. In the range 89–200 K, T_1 in C8d_3-MC was longer than that in C8-MC, while these T_1 values became close to each other above 200 K.

The T_1 data in C8-MC observed below 200 K can be expressed by the superposition of two BPP-type relaxation rates,

$$T_1^{-1} = T_{1a}^{-1} + T_{1b}^{-1}, \tag{1}$$

each of which is expressed as [7]

$$\frac{1}{T_1} = \frac{2}{3}\gamma^2 \Delta M_2 \left\{ \frac{\tau}{1+(\omega_0 \tau)^2} + \frac{4\tau}{1+(2\omega_0 \tau)^2} \right\}, \tag{2}$$

where γ, ΔM_2, and ω_0 are the gyromagnetic ratio of a proton, the difference in the second moment of the ^{1}H NMR line-width before and after the onset of the motion, and the angular Larmor frequency, respectively. We assume an Arrhenius-type relationship between the correlation time τ and the activation energy E_a of the motion:

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right). \tag{3}$$

Referring to the ^{2}H QCC analysis given above, the T_1 minimum observed at 300 K was attributed to the reorientation of *n*-octylammonium ions about their long axis in unequal potential wells for two reasons. The first is that, in the temperature range where the T_1 minimum was observed, ^{2}H QCC in C8d_3-MC is still in the process of narrowing and not narrowed to the theoretical value for this uniaxial rotation. This contradicts the consideration of a single excitation process in which motional time scales for the spectrum narrowing and the T_1 minimum are quite different. The second one is that a ΔM_2 of 6 G^2 derived from the T_1 value of 72 ms at the minimum observed at 48.9 MHz is too small compared to 10.5 G^2 calculated for the cationic uniaxial reorientation between the equivalent potential wells. This is because an increase of the T_1 minimum is expected for motions in an asymmetric potential well, as discussed below.

Above 250 K it is assumed that the cations experience four equilibrium orientations obtainable by successive 90° rotations about the long axis, as illustrated in Figure 5. These four positions are labelled in turn by 1, 2, 1′, and 2′, where the potential depths at 1 and 1′ or 2 and 2′ can be regarded as almost the same. The activation barriers from the positions 1 and 2 are expressed as E_{a1} and E_{a2} ($E_{a1} > E_{a2}$), respectively, as shown in Figure 5. The theoretical T_1 curve for this asymmetric potential model is given by [8]

$$\frac{1}{T_1} = \frac{2}{3}\gamma^2 \Delta M_2 \left\{ \frac{4\varepsilon}{(1+\varepsilon)^2} \right\} \cdot \left\{ \frac{\tau}{1+(\omega_0 \tau)^2} + \frac{4\tau}{1+(2\omega_0 \tau)^2} \right\}, \tag{4}$$

where

$$\varepsilon = \exp\left(\frac{E_{a2} - E_{a1}}{RT}\right) \tag{5}$$

and

$$\tau = \tau_0 \left(\frac{2}{1+\varepsilon}\right) \exp\left(\frac{E_{a1}}{RT}\right). \tag{6}$$

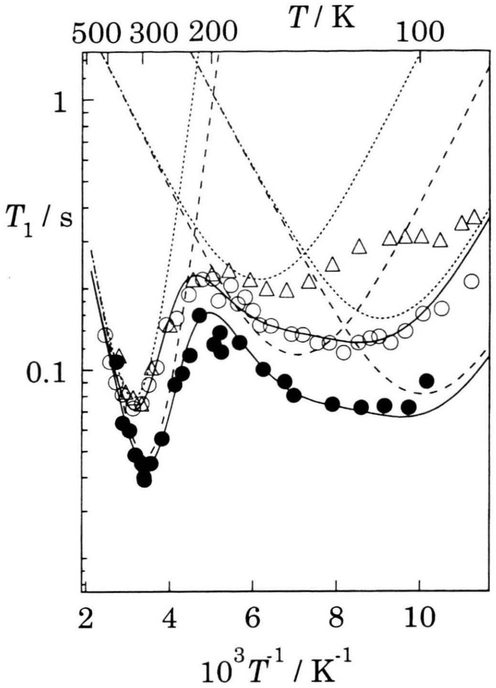

Fig. 6. The temperature dependence of the ^{1}H NMR spin-lattice relaxation time T_1 observed at Larmor frequencies of 48.9 (○) and 25.6 MHz (●) in n-$C_8H_{17}NH_3$-mica (C8-MC), and at 48.9 MHz (△) in n-$C_8H_{17}ND_3$-mica. Solid lines indicate the best fitted theoretical values in C8-MC and broken and dotted lines are T_1 components calculated at 48.9 and 25.6 MHz in C8-MC, respectively.

Table 2. Motional modes, activation energies (E_{a1}), reductions of second moments (ΔM_2) and the difference of the potential depths ($\Delta = E_{a1} - E_{a2}$) derived from ^{1}H NMR spin-lattice relaxation times (T_1) observed in n-$C_8H_{17}NH_3$-mica.

Motional Mode	E_{a1}/kJ mol^{-1}	ΔM_2/G^2	Δ/kJ mol^{-1}
NH_3^+-rot	5.5 ± 1	2.9 ± 0.5	
CH_3-tumbling	5.9 ± 1	2.1 ± 0.5	
Chain-rot	27 ± 2	11 ± 2	5.0 ± 1

The best fitted T_1 curves and determined motional parameters are shown in Fig. 6 and Table 2, respectively. The asymmetric potential model is acceptable in this system because ΔM_2 of 11±2 G^2 derived from the minimum observed at 300 K agrees with the value of 10.5 G^2 calculated for the uniaxial rotation.

By the ^{2}H QCC analysis it was shown that NH_3^+ reorientation occurs below ca. 100 K. We can reasonably assign the minimum observed at about 100 K to the NH_3^+ reorientation about the C_3 axis, because the observed T_1 in C8d_3-MC in this temperature range is much longer than T_1 in C8-MC, as is explainable by the effect of the NH_3^+ deuteration. The fact that the ΔM_2 of 2.9 G^2 obtained for the C_3 rotation of NH_3^+ was smaller than 3.7 G^2 calculated for this motion indicates that the motional correlation time seems to be somewhat distributed because of the heterogeneous circumstance made by the charge distribution in clay sheets of mica. The other T_1 minimum observed at ca. 150 K seems to be attributed to tumbling motions of the CH_3 ends in the layer plane with the fixed NH_3^+ ends. This is because the ^{2}H QCC showed only NH_3^+ reorientation below this T_1 minimum temperature.

In the temperature range up to 410 K we observed no T_1 decrease corresponding to the narrowed ^{2}H spectrum observed at 480 K, presumably because the T_1 due to in-plane tumbling of the whole cation giving the ^{2}H spectrum narrowing is too long to be detected below 410 K.

Conclusions

Motional states of *n*-octylammonium ions intercalated in mica were shown to be quite different from those in pure crystalline *n*-alkylammonium halides. The activation energy of 5.0 ± 1 kJ mol^{-1} for the NH_3^+ rotation in C8-MC is much smaller than 23, 26.8, 28 and 13.0 kJ mol^{-1} determined in n-$C_4H_9NH_3Br$ [9], n-$C_4H_9NH_3$ [10], n-$C_5H_{11}NH_3Cl$ [11], and n-$C_{12}H_{25}NH_3Cl$ [12], respectively. Clay layers in which negative charges are dispersed seem to attract the NH_3^+ more loosely than the halide anions with concentrated charges.

It is noted that E_{a1} of 27 ± 2 kJ mol^{-1} determined for the uniaxial rotation of intercalated ions as a whole is much larger than 5 – 18 kJ mol^{-1} of the same mode in *n*-alkylammonium salts [9, 12] in the tetragonal crystalline phase. The high E_a for this ionic motion in the clay can be explained by the movable space of ca. 0.4 nm width in the interlayer of the clay, smaller than ca. 0.5 nm estimated in pure crystals [12].

As a new kind of 2-D cationic motion, we found the in-plane tumbling of cations as a whole about axes perpendicular to the molecular axis in the high-temperature range above 450 K. The 2-D space formed by clay sheets enables this new type of 2-D motion, which could not so far be found in bulk crystals.

We can compare the present results with those obtained in *n*-octylammonium-saponite, abbreviated C8-SP. In both C8-SP and C8-MC, analogous motional modes of the intercalated ions, i.e., NH_3^+ and uniaxial reorientations and in-plane tumbling as a whole were observed, but they showed different dynamic properties: The first difference is that the excitation of cationic motions in C8-SP occurs at higher temperatures than in C8-MC, implying that the motional barrier in saponite is higher than in mica. This can be explained by the difference in distances between anionic and cationic centres, i.e., the anions in saponite are located on the inner surface made by SiO_4 tetrahedra, whereas charges in mica from MgO_4F_2 octahedral sites are separated from intercalated ions by silicate layers. As the second difference, dynamic properties of intercalated ions in C8-SP are characterised by a distributed motional correlation time, attributable to the small crystal sizes of saponite and heterogeneously distributed negative charges in the clay wall. On the other hand, it was found in C8-MC that the cationic uniaxial rotation could be explained without τ distribution, and this can be expected from crystal sizes of mica large enough to form homogeneous circumstance over most of the intercalated ions. These results suggest that the dynamic properties of intercalated ions in clays markedly depend on the clay structure.

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