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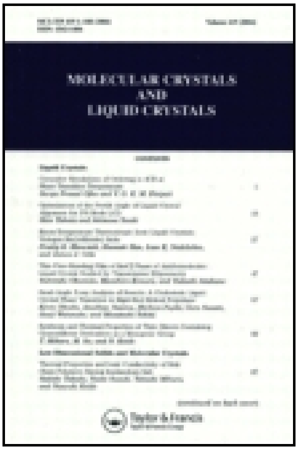

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Dynamics of n-Octylammonium Ions Intercalated in Saponite

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Dynamics of n-Octylammonium Ions Intercalated in Saponite

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(In final form June 25, 1999)

Dynamic behavior of n-octylammonium ions intercalated into saponite was investigated by ^{2}H and ^{1}H solid NMR method. Obtained data indicate distributions in the rate of cationic axial reorientations characterized by the heterogeneity of charge distribution in the saponite layer plane. Above ca. 400 K, in-plane random reorientations of cations were observed as a new kind of motion in the 2-D ionic system.

Keywords: solid state NMR; n-octylammonium; saponite; T_1; quadrupole coupling constant

INTODUCTION

It has been reported[1] that n-alkylammonium ions can be intercalated into layered clay minerals carrying negative charges in the wall, and, in clays with a low concentration of layer charges such as smectites, cations are arranged with their long axes parallel to the sheet. Since anionic sites in the wall are randomly located in clays, obtained alkylammonium systems can be regarded as two-dimensional cationic aggregates with randomly distributed positions as well as orientations. Our interest is the dynamic behavior in such two-dimensional systems and, in the present study, we intend to inv

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EXPERIMENTAL

Intercalation of n-octylammonium ions into Na-saponite (a reference clay of the Clay Society of Japan, JCSS-3501) was performed by the ion exchange method. Obtained n-$C_8H_{17}NH_3$-saponite, and a deuterated analog, n-$C_8H_{17}ND_3$-saponite, are hereafter designated C8-SP and C8d_3-SP, respectively. Identification of C8-SP was carried out by elemental analysis and powder X-ray diffraction (XRD). ^{2}H NMR spectra in C8d_3-SP were observed at a Larmor frequency of 46.05 MHz with a Bruker MSL-300 NMR system. ^{1}H NMR spin-lattice relaxation times (T_1) in C8-SP and C8d_3-SP were determined with a home-made apparatus at 50.4 and 23.5 MHz, and 48.9 MHz, respectively.

RESULTS AND DISCUSSION

Sample Identification

The interlayer distance in C8-SP obtained by subtracting the layer thickness 0.96 nm[2] from *d*-spacing of the (001) peak of XRD patterns observed in C8-SP was 0.4±0.1 nm, indicating that n-octylammonium ions are intercalated into saponite and arranged their long axes parallel to the clay layers.

The elemental analysis in C8-SP showed that 58 % of Na in Na-SP was exchanged with n-octylammonium cations implying that the available area for a cation was ca. 0.75 nm^2. Since the area of a flat-lying n-octylammonium ion, ca. 0.60 nm^2 is close to 0.75 nm^2, we can presume that a two-dimensional phase of densely packed n-octylammonium ions was formed between the saponite layers.

NMR Measurements

^{2}H NMR spectra observed in a temperature range 116-480 K were shown to consist 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 the presence of several kinds of n-octylammonium ions in different motional states, namely, the sharp and broad components in the spectra originate from mobile and restricted ions,

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respectively. Quadrupole coupling constants (QCC) determined from the linewidth of the broad component of ^{2}H spectra are shown in Fig. 2. The QCC of 50±5 kHz obtained at 116 K was smaller than 58 kHz calculated for rotating ND_3^+ groups about the C_3 axis derived from 173 kHz observed in rigid $C_2H_5ND_3^+$[3], indicating that this motional mode has already been excited below 116 K. Over a wide range 116-400 K, QCC gradually decreased from 50 to 20 ± 10 kHz being smaller than 22 kHz calculated for the model of the cationic uniaxial rotation about its long axis. This unusually gradual reduction suggests that the reorientational correlation time of the uniaxial rotation is widely distributed. 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 because of the narrowed width of ca. 5 kHz observed in this temperature region.

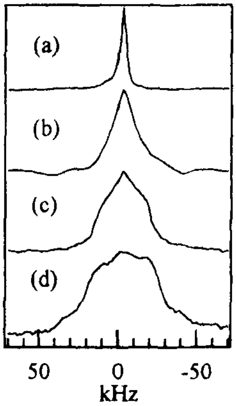

FIGURE 1 ^{2}H NMR spectra in C8-SP at 480 K(a), 380 K(b), 340 K(c) and 116 K(d).

The ^{1}H NMR spin-lattice relaxation times (T_1) measured in C8-SP and C8d_3-SP are shown in Fig. 3. We observed a broad and a sharp minimum around 150 and 450 K, respectively. The T_1 data in C8-SP and C8d_3-SP were nearly the same in the whole temperature range studied except for the range 160-300 K, where T_1 in C8d_3-SP was longer than those in C8-SP. This implies that the broad T_1 minimum consists of two minima: one in the high-

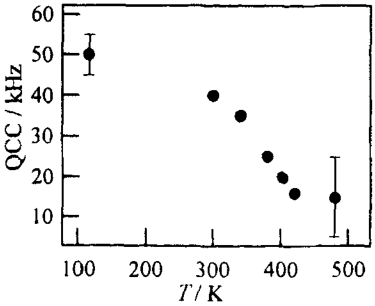

FIGURE 2 Temperature dependence of ^{2}H quadrupole coupling constant.

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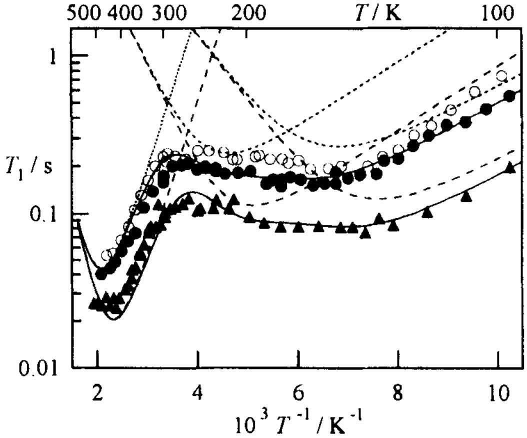

FIGURE 3 ^{1}H NMR spin-latticerelaxation times T_1 observed at 50.4 MHz(●) and 23.5 MHz (▲) in C8-SP, and at 48.9 MHz (○) in C8d_3-SP. The lines denote values calculated by introducing distributions in correlation times. See text.

temperature region, which was affected by the deuteration, is attributable to a motion of NH_3^+ groups, while the other in low-temperatures can be explained by the CH_3 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[4]. 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 NH_3^+- and uniaxial rotations are 0.13 and 0.021 s, respectively. Here, we introduce a distribution in the correlation time τ to explain these shallow minimum values and, at the same time, the gradual reduction of QCC. Assuming the Cole-Davidson type distribution[5] given by

$$g(\tau) = \frac{\sin \beta\pi}{\pi}\left(\frac{\tau}{\tau_0 - \tau}\right)^{\beta} \qquad \tau \le \tau_0 \text{ , or} \qquad = 0 \qquad \tau > \tau_0 \qquad (1),$$

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

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

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

$$\tau = \tau_\infty \exp\left[\frac{E_a}{RT}\right] \qquad (3),$$

where E_a is the activation energy and τ_∞ is the correlation time in the limit of infinite temperature. The observed T_1 data in C8-SP were fitted by the superposition of three theoretical curves calculated by using Eqs. (1)-(3), as shown in Fig. 2, where 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. The motional parameters determined by the fitting are shown in Table 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 1. It is noted that the intramolecular motions as well as the overall uniaxial rotation are characterized by the distributed correlation times. E_a of 27 kJ mol^{-1} for the uniaxial rotation in C8-SP is much larger than 5-18 kJ mol^{-1} reported for rotator phases in n-alkylammonium salts[6, 7], where the axial rotation of the whole cations is excited. These results can be explained by the differences in space available for the cationic motion; i.e., the spacing between clay sheets is ca. 0.4 nm in C8-SP, while the spacing for the rotation in the rotator phase has been reported ca. 0.55 nm in n-dodecylammonium chloride[7].

The heterogeneity observed in n-octylammonium motions expected to be caused by the inhomogeneous charge distribution in clay layers. This result and the high E_a for cationic rotations imply that dynamic properties of n-

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octylammonium ions in saponite are strongly influenced by clay's nature. On the other hand, the ^{2}H spectra observed above 400 K in C8d_3-SP are narrowed to ca. 5 kHz, being smaller than ca.15 kHz observed in the rotator phase of deuterated n-dodecylammonium chloride[7]. This implies that the order parameter giving the degree of dynamic distribution of the cationic axis orientation becomes ca. 0.23 in the present system much smaller than ca. 0.6 in the rotator phase of $C_{12}H_{25}NH_3Cl$. This in-plain cationic reorientation can be regarded as a characteristic new mode of motion in the layered clay minerals.

TABLE 1 The fitting parameters of ^{1}H NMR spin-lattice relaxation time. The values in parentheses show those calculated by BPP theory.

Motional Mode	E_a / kJ mol^{-1}	ΔM_2 / G^2	β
CH_3-rot	8.0±0.4	2.7±0.2(2.5)	0.4±0.2
NH_3^+-rot	13±0.5	3.6±0.4(3.7)	0.3±0.2
uniaxial-rot	27±2	12±1(10.5)	0.7±0.1

Acknowledgment

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