NMR Studies on Dynamics of Water Intercalated in Clay Minerals

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The dynamics of water molecules intercalated in D_2O saturated synthetic and natural smectites, and a synthetic Na-fluormica were studied by measurements of solid state ^{2}H NMR spectra and spin-lattice relaxation times at 150 − 370 K. The obtained results could be explained by the 2-site flip, the C_2 rotation and the isotropic rotation of the D_2O molecules in smectites. In fluormica, the isotropic motion was undetectable, but the axial rotation of the hydration sphere as a whole was observed. The activation energies and correlation times of the C_2 rotation were almost independent of the interlayer cations but depended on the character of clay-layers.

Key words: Clay Minerals; NMR; Intercalated Water; T_1.

Introduction

Layer-structured clay minerals have been characterised by their large adsorption capacity in the interlayer space and by the fact that their adsorption character can be modified by the charge density of clay layer and interlayer cations. Since molecules adsorbed in the two-dimensional space are expected to behave differently from those in the bulk state, their dynamic properties have extensively been studied. As a typical adsorbent, the structure and dynamics of water in clay minerals have been investigated by various methods [1, 2], *e.g.*, measurements of thermodynamic parameters [3 - 5], neutron diffraction [6], quasielastic neutron scattering (QENS) [7 - 9] and NMR [10 - 15], and simulations of force field [16], Monte Carlo (MC) [17] and molecular dynamics (MD) [18].

In highly charged clays, such as Na-vermiculite, adsorbed water molecules form an octahedral hydration shell around a cation [16]. In the case of low charged clays, such as montmorillonite, however, adsorbed water molecules can be located not only around the cations but in the interstitial space. This complicated water-environment makes the analysis of the experimental data difficult, and this problem is also caused by the disordered structure in clay minerals, such as inhomogeneity of the charge distribution, stacking defaults in the layers, and considerable effects from surface edges resulting from fine sizes.

Previously we reported ^{2}H and ^{7}Li NMR studies on D_2O saturated synthetic Li-saponite and discussed D_2O motions and the local structure around cations over a wide temperature range [19]. In this study, we perform measurements of ^{2}H NMR spectra and spin-lattice relaxation times (T_1) of six kinds of D_2O saturated clay minerals and attempt to reveal effects of cations and clay-layer on dynamics of adsorbed water molecules.

We selected the following synthetic clays for NMR measurements to avoid the influence from paramagnetic impurities: Na-fluormica, Na-hectorite, Na-saponite, Cs-saponite and tetramethylammonium-(TMA)-saponite. A natural clay, Tsukinuno Na-montmorillonite containing 19,300 ppm Fe, was also used for comparison.

Experimental

Synthetic Na-saponite ($Na_{0.4}Si_{3.6}Al_{0.4}Mg_3(OH)_2O_{10}$) being a reference clay (JCSS-3501) of the Clay Science Society of Japan (CSSJ), synthesized by Kunimine Industries Co., Ltd was obtained from CSSJ. The synthetic clays Na-hectorite ($Na_{0.4}Si_4Mg_{3.1}Li_{0.3}(OH)_2O_{10}$) and Na-tetrasilicicfluormica ($Na_{0.75}Si_4Mg_{2.7}F_{0.85}(OH)_{1.2}O_{10}$) were kindly gifted from CO-OP Chemical Co., Ltd. A natural Yamagata Tsukinuno montmorillonite ($Na_{0.3}Si_4Al_{1.7}Mg_{0.3}(OH)_2O_{10}$) was given by Kunimine Industries Co., Ltd.

Cs and TMA-saponites were prepared by the standard cation exchange method from Na-saponite using

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a 2 mol dm^{-3} CsCl and a TMACl aqueous solution, respectively. The suspensions of the cation exchanged clays were filtered and washed with distilled water until the filtrates showed negative reaction to the $AgNO_3$ test.

The specimens for NMR measurements were put in glass tubes and aspirated at room temperature for one day, then exposed to D_2O vapour at its saturated vapour pressure at room temperature. These specimens were then sealed with helium gas of atmospheric pressure. The D_2O contents in these specimens were determined by the weight loss after heating to 200 °C.

The ^{2}H NMR spectra and T_1 were measured with a Bruker MSL-300 NMR system at 150 - 370 K. The temperature was controlled within ±5 K. The evaluated error in the T_1 measurement was ±10%.

Results and Discussion

X-Ray Diffraction and Gravimetric Analysis

The X-ray diffraction of powdered smectites showed diffused patterns, while Na-fluormica gave sharp peaks. The determined $d(001)$ spacings and D_2O contents per cation of each clay are listed in Table 1. The D_2O contents determined in alkali metal clays, except for Na-fluormica, were large compared with the accepted hydration numbers of $\leq 6 \sim 10$ for the cations in aqueous solution [20], and 6 for vermiculite [13], implying the existence of non-hydrated water molecules in the interstitial space of the clay layers. On the other hand, 14 D_2O molecules per TMA cation is considered to be not many for a large cation, suggesting that the D_2O molecules are in the first hydration sphere, although the interaction between the TMA cation and water molecules is so weak that it is difficult to specify the hydration number. Na-fluormica, known as a highly charged mineral with few interstitial sites, showed a small number, 6.7, corresponding to the normal hydration number of 6 for an Na^+ cation.

Table 1. D_2O contents and X-ray $d(001)$ spacings in D_2O saturated clays.

Clay	D_2O molecules / cation	$d(001)$ spacing / nm
Na-saponite	15.8 ± 0.2	1.38 ± 0.1
Cs-saponite	26.0 ± 0.2	1.37 ± 0.1
TMA-saponite	14.0 ± 0.2	1.56 ± 0.1
Na-hectorite	14.9 ± 0.2	1.42 ± 0.1
Na-montmorillonite	19.4 ± 0.2	1.50 ± 0.1
Na-fluormica	6.7 ± 0.1	1.24 ± 0.02

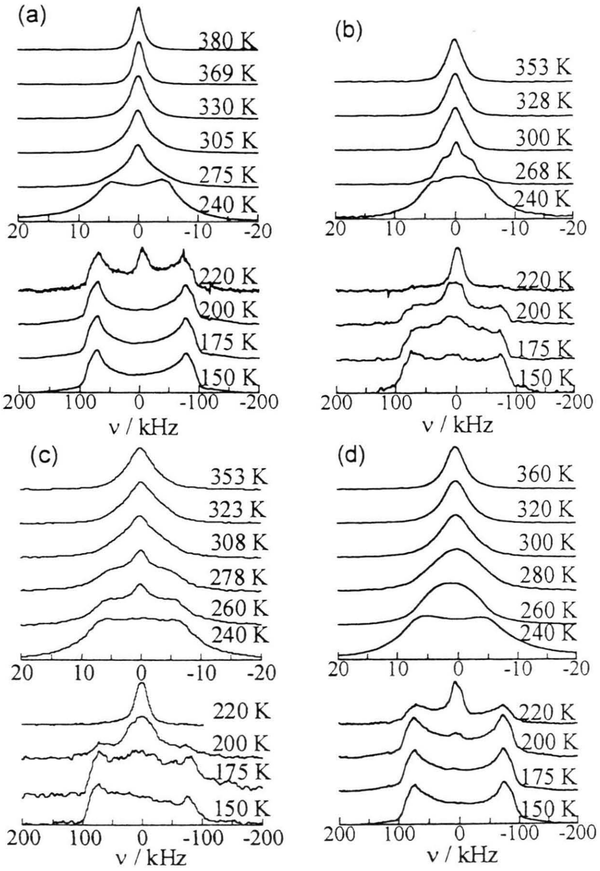

Fig. 1. Temperature dependences of ^{2}H NMR spectra in D_2O saturated Na-saponite (a), Cs-saponite (b), TMA-saponite (c), and Na-hectorite (d).

^{2}H NMR Spectra

Temperature dependences of the ^{2}H NMR spectra in cation replaced saponites and Na-hectorite are shown in Figure 1. Their common behaviour can be roughly summarized as follows: Estimated quadrupole coupling constants (e^2Qq/h) of *ca.* 220 kHz observed in each sample at 150 K agree with 220 kHz for the rigid water determined in Li-saponite [19]. Upon heating, a sharp component appeared at the centre of each spectrum at 200 - 220 K, then, on heating to 240 K, the spectra became a single central absorption line of a doublet structure with a width of *ca.* 20 kHz, assignable to D_2O molecules rotating about their C_2 axis [13]. Above 300 K, each

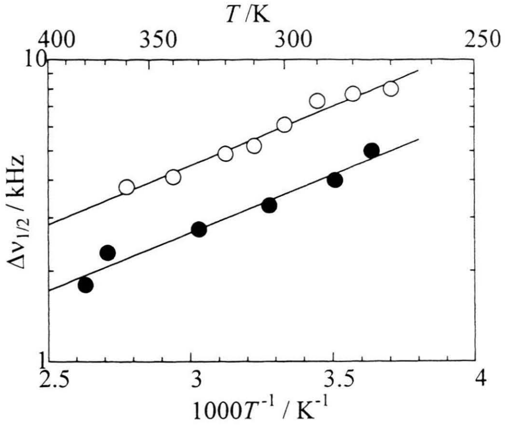

Fig. 2. Temperature dependences of ^{2}H NMR line-widths ($\Delta\nu_{1/2}$) in D_2O saturated Na-saponite (●) and Na-hectorite (○) observed above 270 K. Sold lines are best fitted Arrhenius relations.

clay showed a structureless sharp peak corresponding to isotropically rotating D_2O molecules.

On detailed observations, the spectrum changes in Na-saponite and Na-hectorite, resembling each other, differ somewhat from those in Cs and TMA-saponites. The two Na-clays showed well defined rigid spectra up to 200 K, whereas the central peak already appeared at 175 K in the latter two clays, implying that the water molecules are more tightly bounded in the Na-clays at low temperatures.

The structure of the central line almost disappeared around 300 K in the Na-saponite, hectorite, and Cs-saponite spectra, but it remained a little even at 323 K in TMA-saponite. The sharp central ^{2}H line observed at high temperatures indicates that the environment of a hydrogen atom becomes isotropic in the NMR time scale if it jumps among the four tetrahedral sites, because water molecules have tetrahedral symmetry on average in the bulk liquid. As mentioned above, the D_2O contents in Na- and Cs-smectites (Table 1) are sufficiently high compared with the coordination number of each cation, while this is not the case in the TMA-saponite. These facts suggest that the water molecules make hydrogen-bond networks in Na- and Cs-smectites as in bulk-water but form isolated hydration spheres in TMA-saponite.

Finally, the line-width of the structureless peak observed in Na-saponite and hectorite was found to be temperature dependent above 270 K (Figure 2). This reduction of the line-width can be attributed to the averaging of the electric field gradient (EFG) by the diffusional motion of the D_2O molecules such as the exchange between hydrate and free molecules. The similar slope of the temperature dependences of the line-width obtained in Na-saponite and hectorite shown in Fig. 2 suggests that this motion has the same activation energy in these two clays.

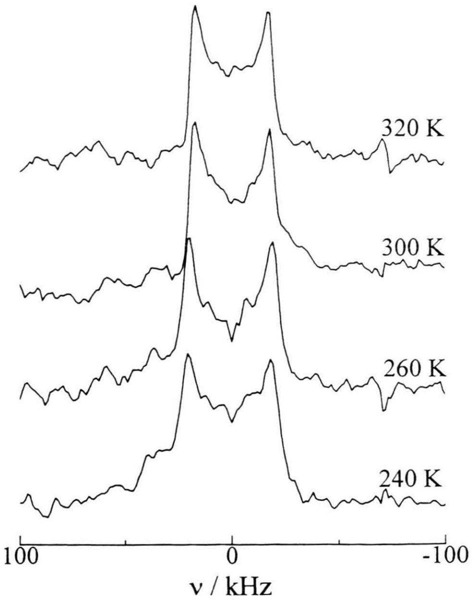

Fig. 3. A temperature dependence of the ^{2}H NMR spectrum in D_2O saturated Na-fluormica.

Cs-Saponite did not show such a reduction in line-width at high temperatures. We can propose two possible mechanisms for this observation; **1.** the large Cs-ion produces a small EFG at hydrate D_2O molecules and **2.** the cationic diffusion rate is already fast enough to average out the residual EFG in this temperature region because of the low activation energy of water-exchange caused by the negative hydration effect [21].

As shown in Fig. 3, temperature-independent ^{2}H NMR spectra were observed in Na-fluormica above 260 K. The obtained $e^2Qq/h = 60 \pm 2$ kHz and asymmetric parameter $\eta \simeq 0$ are explainable by the rotation of a D_2O molecule about an axis, tilted by 61° from the molecular C_2 axis accompanied by a 180°-flip around the C_2 axis. This angle 61° agrees well with 65° [13] reported for the angle between the C_3 axis of the octahedral hydration shell around the Na^+ and the C_2 axis of water molecules in Na-vermiculite.

^{2}H NMR spectra were also measured in natural Na-montmorillonite but cannot be interpreted because

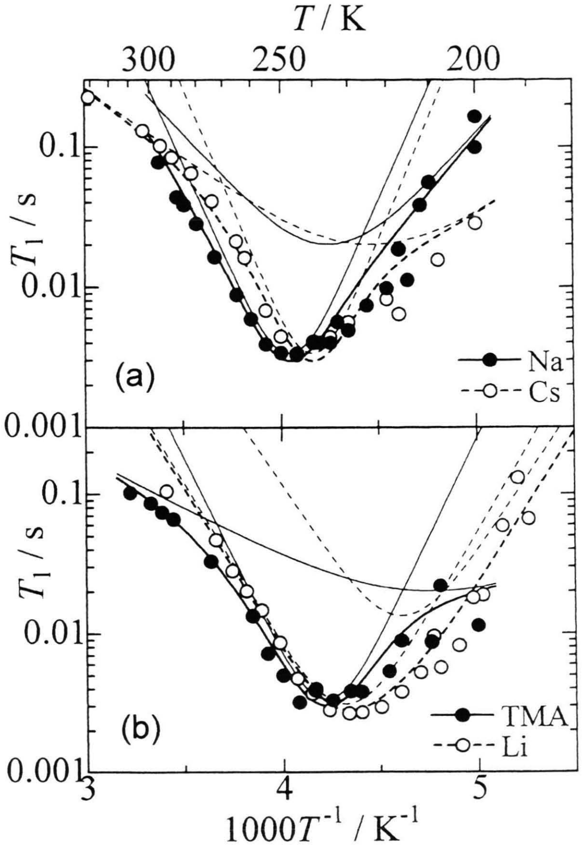

Fig. 4. Temperature dependences of ^{2}H NMR spin-lattice relaxation times (T_1) in D_2O saturated Na- (●) and Cs- (△) (a) and TMA- (×) saponites and previously reported Li-saponite (○) (b). Bold lines represent the best-fitted calculated values for $(T_1)_{net}$, and thin lines for $(T_1)_{mode\,1}$ and $(T_1)_{mode\,2}$.

the spectra were highly deformed probably owing to paramagnetic impurities such as Fe^{2+} and Fe^{3+}.

^{2}H NMR Relaxation Time

Figures 4 and 5 are the cation and host clay dependences, respectively, of the ^{2}H NMR T_1. Each specimen showed a T_1 minimum at 230 - 240 K. The slopes of the temperature dependences were asymmetric above and below the minimum.

The observed relaxation rate T_1^{-1} could be reproduced by adding contributions from two motional modes **1** and **2** for deep and shallow minima, respectively:

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

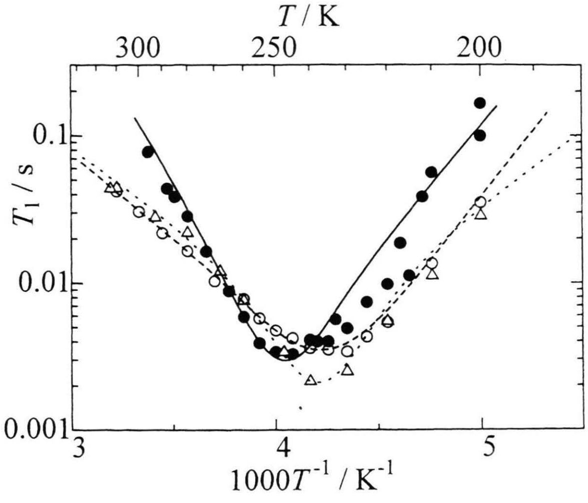

Fig. 5. Temperature dependences of ^{2}H NMR spin-lattice relaxation times (T_1) in D_2O saturated Na-saponite (●), hectorite (○) and Tsukinuno montmorillonite (△). The best-fitted $(T_1)_{net}$ are given by — for Na-saponite, - - - for hectorite, and · · · for montmorillonite.

The T_1^{-1} for each mode is represented by a BPP-type equation [22]:

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

as an ordinary thermal relaxation, where C is the parameter determined by the reduction of the quadrupole coupling constant, $\Delta e^2Qq/h$, by the excitation of the motion, ω is the ^{2}H Larmor frequency, and τ is the correlation time of the motion given by the Arrhenius equation

$$\tau = \tau_0 \exp(E_a/RT), \tag{3}$$

where E_a is the activation energy of the motion.

Table 2. Motional constants (C) and activation energies (E_a) for the modes **1** and **2** in D_2O molecules derived from observed ^{2}H NMR T_1 data.

Clay	C / 10^{10} s^{-2} mode **1**	C / 10^{10} s^{-2} mode **2**	E_a / kJ mol^{-1} mode **1**	E_a / kJ mol^{-1} mode **2**
Na-saponite	6.0 ± 0.6	1.0 ± 0.2	60 ± 3	29 ± 3
Cs-saponite	6.0 ± 0.6	1.0 ± 0.2	65 ± 3	19 ± 2
TMA-saponite	6.0 ± 0.6	1.0 ± 0.2	55 ± 3	14 ± 1
Li-saponite*	6.5 ± 0.6	1.5 ± 0.3	45 ± 2	40 ± 3
Na-hectorite	5.5 ± 0.5	0.5 ± 0.1	35 ± 2	20 ± 2
Na-montmorillonite	8.0 ± 0.8	1.7 ± 0.3	60 ± 3	19 ± 2

* Re-fitted values for previously reported T_1 data [19].

Equations (1) - (3) were fitted to T_1 data in Figs. 4 and 5. The best-fitted parameters for each specimen are listed in Table 2. Re-fitted parameters for Li-saponite, whose T_1 was previously fitted by a single motion [19], are also listed together.

Asymmetric T_1 curves observed in the present systems have often been analysed by introducing models of τ-distribution [14, 15] as reported in complex systems such as glasses, polymers and intercalation compounds. We also tried to apply several models of this type, but obtained unsuccessful results: The observed T_1 minima, which markedly depend on the degree of τ-distribution, are almost equal except for Na-montmollironite, despite the different degrees of asymmetry in T_1 curves. The other reason is that $\Delta e^2Qq/h$ of 300 - 330 kHz, derived from T_1 minimum values in Cs- and TMA-saponite using the τ-distribution model, is unacceptably large to be attributed to D_2O motions, which give at most 230 kHz [23, 24] even for the rigid water molecules rotating isotropically.

As for mode **1**, the C values coincided within experimental errors except for Na-montmorillonite, suggesting that we observed the same motion in these clays. From the determined C values, neglecting the contribution from η, the $\Delta e^2Qq/h$ caused by the motion was estimated to be 200 ± 20 kHz [19]. The larger C value in Na-montmollironite than in the other diamagnetic systems is explainable by the contribution from dipole-dipole interactions between ^{2}H nuclei and unpaired electrons. On the other hand, it is difficult to attribute the C values for mode **2** to the same motion because they have much ambiguity and disperse in a range of $0.5 - 1.5\times10^{10}$ s^2.

Around the T_1 minimum, the τ of the concerning motion becomes nearly equal to the ^{2}H Larmor frequency, while the same motion affects the NMR line-shape at the temperature where τ approaches the line-width, *i.e.*, 10 $\sim$ 100 kHz. We can, accordingly, estimate the temperature where the spectral change is observed, provided the T_1 minimum temperature and the activation energy are obtained. Applying this procedure, the spectral changes at *ca.* 200 K can be connected with mode **1** in all clays. Thus we can assign mode **1** to the C_2 rotation of D_2O molecules because, as shown in Fig. 1, a reduction of the linewidth attributed to the C_2 rotation was recognized around 220 K. Analogous narrowings for mode **2** are expected below 150 K in Cs- and TMA-saponites, and near 180 K in Na-saponite and hectorite. A central component explainable by a large η was observed at 150 - 200 K in the former two clays. This spectral change can be assigned to the 2-site flipping motion. On the other hand, any evident spectral change was absent in the latter two clays below 200 K, probably because the narrowing is overlapped with that of mode **1**.

The E_a value of mode **1** seems to be insensitive to the kind of cation but sensitive to the character of the clay-layers. This fact also supports our assignment of mode **1** to the C_2 rotation which is more susceptible to interactions between D_2O and the clay surface and/or hydrogen-bonds among D_2O molecules than to cation-water interaction. The E_a difference in saponites and hectorite can be explained by the position of the anionic centres in the clay-layer: Saponite and hectorite have isomorphic structures, but the anionic centre is placed at the layer surface in saponite, but at the centre of the layer in hectorite. The longer distance between the charge centre and the D_2O molecules in hectorite is expected to lead the weaker interaction, *i.e.*, the lower E_a. In montmorillonite, however, a high E_a of 60 kJ mol^{-1} was obtained although the anionic centres are at the inside of the layer. The fact that the montmorillonite has a bioctahedral layer structure [25] may give rise to the difference in E_a from that of the trioctahedral clays saponite and hectorite.

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