

NMR Studies on the Dynamics of Intercalated Water in Li-saponite

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Z. Naturforsch. **52 a**, 863–866 (1997); received August 19, 1997

The dynamics of intercalated water molecules in Li-saponite was studied by measurement of solid state ^2H and ^7Li NMR spectra and of the ^2H spin-lattice relaxation time at 175 ~ 350 K. Only a single component was observed in the ^2H spectra above 260 K, suggesting that the water hydrogens rapidly exchange their positions between various distinct environments. Analysis of the observed spectra suggests that the water molecules possess C_2 rotational freedom at around 260 K and that the hydration shell around Li^+ cations is highly symmetrical in the same temperature region.

Introduction

Recently, layer-structured clay minerals have attracted great attention due to their intercalating properties [1,2]. Saponite, usually expressed as $\text{M}_x\text{Si}_{4-x}\text{Al}_x\text{Mg}_3(\text{OH})_2\text{O}_{10}$ (M: Li, Na, K, etc.), is a type of layered clay mineral consisting of layers of MgO_6 sandwiched between two sheets of SiO_4 with an analogous layer structure to that of talc, $\text{Si}_4\text{Mg}_3(\text{OH})_2\text{O}_{10}$. The characteristic of this layer system is the carrying of negative charges caused by isomorphic substitution of Si^{4+} with Al^{3+} and, to maintain neutrality, cations are taken up into the interlayer space. This structure enables various polar molecules, such as water, to also be intercalated between the layers.

The structure and dynamics of water in such porous media have attracted attention on account of its peculiarity [1]. The clay minerals are example of such porous media and their hydrated systems have been studied by various methods, e.g., measurement of thermodynamic parameters [3–5], quasielastic neutron scattering (QENS) [6–8] and NMR [9], and simulations by Monte Carlo (MC) [10] and molecular dynamics (MD) [11] methods. In highly hydrated clay, the intercalated water can be classified into several categories corresponding to the strength of its adsorption. This diversity of water environments makes analysis of the experimental data difficult. Spectroscopic methods can observe only motions or struc-

tures which match to the time scale of the observation method. Conversely, computer simulation methods can reproduce well the behaviour of all contained water molecules, but it is difficult to see the (slow) motions of the constituent molecules, and also the size of the system is limited because of problems of calculation time.

To get information about the very slow motion of the order of 10 MHz corresponding to the applied NMR frequencies, expected for water molecules in the clay, we conducted solid state ^2H and ^7Li NMR spectra and ^2H spin-lattice relaxation time (T_1) measurements over a wide temperature range.

Experimental

We used a synthetic Na-saponite, $\text{Na}_{0.4}\text{Si}_{3.6}\text{Al}_{0.4}\text{Mg}_3(\text{OH})_2\text{O}_{10}$, which is a reference clay (JCSS-3501) of the Clay Science Society of Japan as the starting material. Li-saponite was prepared by the standard cation exchange method using a 2 mol l^{-1} LiCl aqueous solution. The suspension of the cation exchanged clay was filtered and washed with distilled water until the filtrate showed a negative reaction to the AgNO_3 test.

The specimens for NMR measurement were put in glass sample 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 under atmospheric pressure. The D_2O content in these specimens was determined by measuring the weight loss after heating to 600°C to be ca. 35 molecules per cation.

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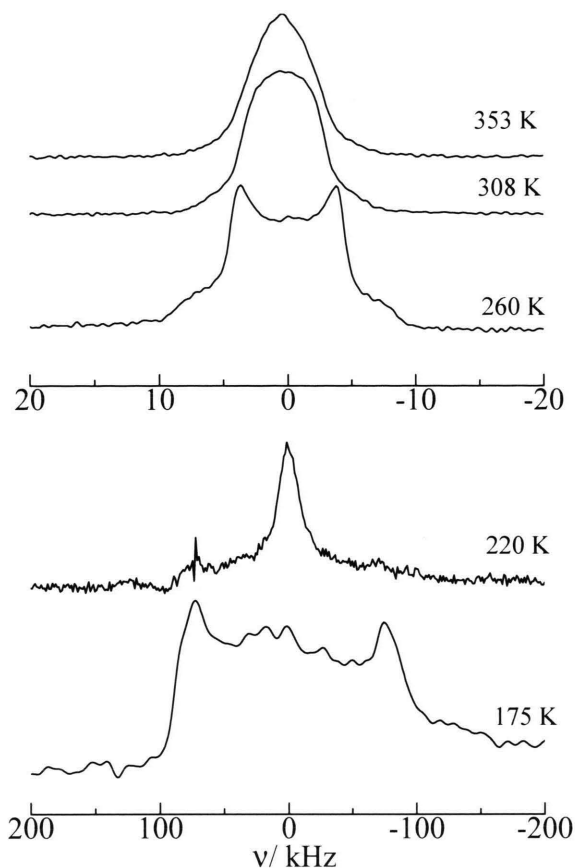


Fig. 1. The temperature dependence of ^2H NMR spectra in D_2O saturated Li-saponite.

^2H and ^7Li NMR spectra and ^2H NMR T_1 were measured using a Bruker MSL-300 NMR system over a temperature range of 175–350 K. The sample temperature reading was controlled within ± 2 K, with its accuracy being estimated to be about ± 5 K. The evaluated error in T_1 was $\pm 10\%$.

Results and Discussion

We determined the size of the interlayer space of the prepared Li-saponite by means of X-ray powder diffraction data. A diffuse peak sited at $d = 1.72 \pm 0.15$ nm was observed at room temperature. The interlayer distance was determined as 0.76 nm by subtracting the 0.96 nm reported as being the pure layer thickness [12] from the observed value. The estimated interlayer distance corresponds to three or more layers of water molecules being present in the interlayer space.

The temperature dependence of the ^2H NMR spectra is shown in Figure 1. The quadrupole coupling constant (e^2Qq/h) and the asymmetry parameter (η) were determined to be 220 ± 5 kHz and 0.10 ± 0.02 at 175 K, respectively. The fact that these values agree well with reported e^2Qq/h values, 213 and 216 kHz, and $\eta = 0.1$, for the rigid water molecules in D_2O -ice [13] implies that the greater part of the interlayer-water freezes below 200 K, where the swelling at the centre of the spectrum shows that some slow motion is occurring even at 175 K.

Upon heating, the ^2H spectrum was drastically sharpened around 220 K. At 260 K, the spectrum shows a well-defined structure again. The e^2Qq/h and η values obtained from this spectrum are 11.0 ± 0.5 kHz and ~ 0 , respectively. This large reduction in the e^2Qq/h value can be attributed to the onset of a single motional process of water molecules by way of the relaxation measurement given below. We can assign this motion to the rotation of D_2O about its C_2 axis since the e^2Qq/h and η values for this motion can be calculated as being 13.8 kHz and 0 [15], respectively, provided we assume e^2Qq/h and η in the rigid molecule to be 220 kHz and 0.1, respectively, and the D-O-D bond angle to be 104.51° [15].

We then eliminated the possibility that a combination of two or more motions of D_2O molecules might explain the observed spectral narrowing by determining the ^2H NMR relaxation time (T_1). Figure 2 shows the observed temperature dependence of T_1 . The ^2H T_1 is governed by a single molecular motion and can

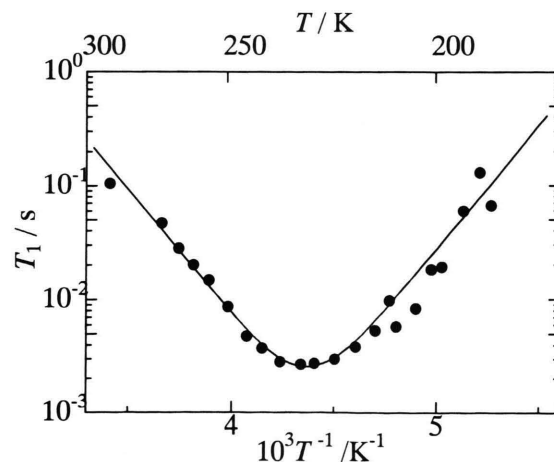


Fig. 2. The temperature dependence of ^2H NMR spin-lattice relaxation time, T_1 in D_2O saturated Li-saponite. The solid line is the best-fit calculated curve. See details in text.

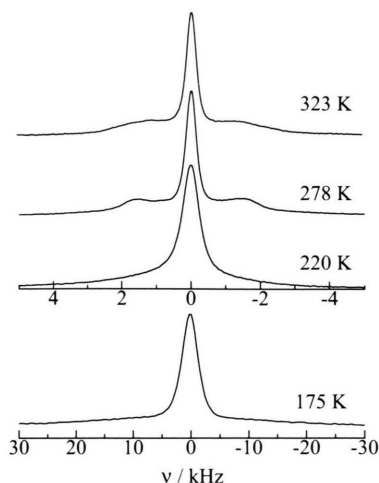


Fig. 3. The temperature dependence of ${}^7\text{Li}$ NMR spectra in D_2O saturated Li-saponite.

be expressed as a BPP type relation [16], given by

$$T_1^{-1} = \frac{3}{80} \left(1 + \frac{\eta^2}{3} \right) \left(\Delta \frac{e^2 Q q}{\hbar} \right)^2 \{ J(\omega_0) + 4J(2\omega_0) \},$$

where $\Delta e^2 Q q / \hbar$ is the decrease in apparent $e^2 Q q / \hbar$ due to motional averaging, and ω_0 is the ${}^2\text{H}$ Larmor frequency. The spectral density $J(\omega)$ is represented by using the correlation time τ of the motion as follows:

$$J(\omega) = \frac{\tau}{1 + \omega^2 \tau^2},$$

where

$$\tau = \tau_0 \exp(E_a / RT).$$

and E_a is the activation energy of the motion.

The observed T_1 data, fitted by these equations, reproduce a BPP curve corresponding to a single motional process, as shown by the solid line in Figure 2. The estimated $\Delta e^2 Q q / \hbar$, 230 ± 20 kHz, is in good agreement with the ca. 210 kHz observed in the present measurement. This implies that the observed motion can be assigned to the C_2 rotation of the water molecules. The estimated E_a and τ_0 for this motion are 42 ± 2 kJ mol $^{-1}$ and 5.6×10^{-19} s.

At the temperatures above 278 K the line-width was reduced again, suggesting that another motion becomes active around this point. The width of ca. 6 kHz observed at 353 K is, however, very wide compared with the value of < 0.1 kHz predicted for bulk

liquid water, considering the nonhomogeneity of the magnetic field.

To obtain further information about the behaviour of the water molecules around the Li^+ ions, we recorded the ${}^7\text{Li}$ NMR spectra shown in Figure 3. The spectrum observed at 278 K shows a typical line-shape, which consists of a central main peak and symmetric side peaks caused by the first order effect of the nuclear quadrupole interaction for $I = 3/2$ nuclei with a small $e^2 Q q / \hbar$. The value $e^2 Q q / \hbar = 6.5 \pm 0.5$ kHz was estimated from the observed separation ($\Delta\nu$) of the two side peaks using the relationship $\Delta\nu = 1/2(e^2 Q q / \hbar)$ for $I = 3/2$ nuclei [16] and assuming $\eta = 0$. The line-shape became indistinct on both heating above and cooling below this temperature. Below 220 K the central line gradually broadened and the side peaks became ambiguous and distributed over a wide range of ca. ± 20 kHz at 175 K. This implies the presence of inhomogeneity in the Li^+ environment.

Lagaly [17–19] has reported that the layer charges of the clays have significant heterogeneity. Considering this charge distribution and the results of the ${}^2\text{H}$ NMR studies, a possible explanation for the observed ${}^7\text{Li}$ spectrum change may be as follows: In the low temperature region, the water molecules are almost rigid and the Li^+ cations are exposed to a high anisotropy and site inhomogeneity. In the medium temperature region, the water molecules undergo C_2 rotation accompanied by the breaking of hydrogen bonds. The small $e^2 Q q / \hbar$ value of 6.5 kHz for ${}^7\text{Li}$ shows that the cations are in (comparatively) highly symmetric environments. The origin of the finite value of $e^2 Q q / \hbar$ can be attributed to the layer charge centres located near the cations or to a slight deformation of the hydration sphere. The fluctuations in the hydration sphere caused by rotational vibration with a large amplitude and/or exchange of the hydrated water with the outer water environments are expected to be significant, the time scale of this motion becomes comparable to the line-width of ${}^7\text{Li}$ or ${}^2\text{H}$, i. e., of the order of 1 kHz, at elevated temperatures.

The interlayeral water in clay can be classified into three categories [11]: 1) bound water, directly coordinated to the cations, 2) unbound water, without direct coordination to the cations, and 3) hole water, forming hydrogen bond with a hydroxyl of the layer in a depression in the layer. The MD simulation [11] has revealed that the mobility of the unbound water at room temperature is similar to that in the

bulk liquid, while the bound water molecules show no displacement during the calculation time. QENS studies, performed on analogous clay-water systems such as Li-montmorillonite [6], also showed that at least part of the water has a high mobility as in the bulk liquid. The observed ^2H NMR spectra, however, exhibited only a single broad component even at room

temperature. This suggests that the three kinds of water molecules perform mutual exchange over a shorter time period than $10^{-3} \sim 10^{-4}$ s at room temperature, although at the present stage we cannot determine whether molecular exchange as a whole or hydrogen transfer makes the dominant contribution to the exchange.

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