Pergamon

Geochimica et Cosmochimica Acta, Vol. 60, No. 2, pp. 265–275, 1996

0016-7037/96 $15.00 + .00

0016-7037(95)00396-7

Interaction of water with clay minerals as studied by ^2H nuclear magnetic resonance spectroscopy

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(*Received December* 28, 1993; *accepted in revised form October* 24, 1995)

Abstract—The interaction of water with a series of Ca^{2+}/Na^+, Ca^{2+}/NH_4^+, and NH_4^+/Na^+-exchanged hectorite and saponite clays in water- and clay-dominated systems was studied using ^2H NMR. Variable-temperature Nuclear Magnetic Resonance (NMR) (in the range of 189–299 K) was also used to determine the frequency of exchange and the rotation activation energy between water molecules hydrating the cations and the free water of the tactoid. The ^2H quadrupolar splitting and spin-lattice relaxation time (T_1) are related to the ratio of clay to adsorbed water in these systems.

In water-dominated systems (where clay/water ratio $\ll 1$), motional averaging occurs between water hydrating the cations and the "free" or bulk water of the tactoid. In these systems, the spin-lattice relaxation time (T_1) is dominated by the relaxation of the "free" water on the external surface of the tactoids and has a value close to that for D_2O (0.436 s), with the rotational correlation time (τ_c) approaching 2.93×10^{-12} s. A more recent article places τ_c at 1.95×10^{-12} s. The clay systems in this study have clay/water ratios (=0.0238 g-clay/mL-D_2O), and the quadrupolar splittings are of the order of 100 Hz or less. Splittings of <100 Hz indicate that approximately 1 water molecule is bound to the clay for every 1.7×10^3 "free" water molecules.

In clay-dominated systems with extremely low water contents (clay/water ratio > 1 g-clay/mL-D_2O), less motional averaging occurs. Rotational correlation times are slower and greater residual quadrupolar splittings are also observed. Increased residual quadrupolar splittings are observed with increasing clay/water ratios. For a Na-exchanged hectorite sample (5.31 g-clay/mL-D_2O), the quadrupolar splittings are of the order of 12 kHz, and for a Na-exchanged saponite (4.05 g-clay/mL-D_2O), the quadrupolar splittings are of the order of 11 kHz. Rotational activation energies (E_a) of 37.8 kJ·mole^{-1} (9.0 kcal·mole^{-1}) for adsorbed water molecules on Na-exchanged hectorite and 27.2 kJ·mole^{-1} (6.5 kcal·mole^{-1}) for Na-exchanged saponite were calculated from spin-lattice relaxation (T_1) measurements. These values compare with calculated activation energies of rotation (8.5 kcal·mole^{-1}) for water of hydration adsorbed to a Na-exchanged vermiculite.

1. INTRODUCTION

High-resolution Nuclear Magnetic Resonance (NMR) spectroscopy has become a valuable tool to investigate the dynamics of cation (Bank et al., 1989; Tokuhiro et al., 1989; Weiss et al., 1990a,b) and water (Woessner, 1974a,b; 1977; 1980; Woessner and Snowden, 1969; Fripiat et al., 1984) interactions with clay minerals. NMR methods can be used to observe the complex interaction of water, cations, and the clay surface in both dry samples and clay-water suspensions. A recent review article (Ohtaki and Radnai, 1993) reviews the literature on the structure and dynamics of the interaction of cations with water, and summarizes the various methods (including spectroscopies: NMR, EXAFS, XANES, Mössbauer, IR, Raman, and Brillouin; and scattering methods: XRD, neutron diffraction, electron diffraction, small-angle X-ray and neutron scattering, and quasi-electron neutron scattering) used to investigate these interactions. Other spectroscopic studies that address the interaction of clays with water include include Sposito et al. (1983), Fu et al. (1990), and Johnston et al. (1992).

The study of the interaction of water with clays using NMR techniques has primarily involved measurements of ^1H and ^2H spin-lattice (T_1) or spin-spin (T_2) relaxation rates, and lineshape analysis of ^1H and ^2H in water molecules adsorbed on clays (Woessner and Snowden, 1969; Hecht and Geissler, 1970, 1973; Hougardy et al., 1976; Woessner, 1980; Sposito and Prost, 1982; Fripiat and Letellier, 1984; Fripiat et al., 1984). Based upon the results of such studies, it is possible to calculate the distribution, orientation, and diffusion rates of water molecules bound to clays.

^2H is a quadrupolar nuclide with spin I = 1 and a quadrupolar moment of $Q = -2.8 \times 10^{-3} \cdot 10^{-28}$ m^2 (Harris, 1986). In the presence of a magnetic field, the quadrupolar coupling constant (QCC) causes the two allowed transitions ($0 \rightarrow 1$ and $-1 \rightarrow 0$) to be nondegenerate. In the absence of time-averaging of the chemical shifts, both of these transitions are observable (Boddenberg, 1987). The ^2H NMR spectrum of 100% D_2O is extremely narrow single resonance, but in the presence of clay minerals, this resonance is split. This splitting of the ^2H resonance among D_2O molecules adsorbed onto clays confirms that water molecules have a preferential orientation on clays with low water contents at temperatures near 298 K (Woessner and Snowden, 1969; Hecht and Geissler, 1970). Recent ^2H and ^{17}O NMR spectra of clay-water sus-

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pensions have been attributed to the orientation of the water molecules adhering to the clay platelets which have oriented in the presence of a magnetic field (Grandjean and Laszlo, 1989a).

Rapid exchange between "free" water and hydration water around cations occurs in these systems at temperatures above ~280 K (Fripiat et al., 1984). As the temperature is lowered below ~280 K, freezing suppresses this exchange (Fripiat et al., 1984).

In addition to previous studies which focused primarily on clay-water suspensions (Grandjean and Laszlo, 1989a,b, 1990, 1991; Delville et al., 1991), we have studied samples which have very low water content (clay/water > 1 g-clay/mL-D_2O). In this way, information can be obtained about the bonding of water with less interference from the "free" water which is present in clay suspensions and gels. We also investigate samples which have similar clay to water ratios as Grandjean and Laszlo (1989a), but also study the interaction of additional cations.

In this report, ^2H high-resolution NMR spectroscopy was used to examine the interaction of water (D_2O) in a number of Na^+, Ca^{2+}, and NH_4^+-exchanged clays and to investigate the factors that affect the ^2H chemical shift. These factors include the amount of water adsorbed to the clay, the type of adsorbed cation, the net negative layer charge, and the location of the layer charge with respect to the adsorbed water molecules.

Phyllosilicates with large layer charges (e.g., the vermiculite and smectite group minerals including montmorillonite, hectorite, saponite, and beidellite) have relatively large exchange capacities which are dominated by cation adsorption in the interlayer. These cations are in general hydrated with water in natural systems. Phyllosilicates that have small layer charges (e.g., kaolinite, pyrophyllite, talc) have a small but finite exchange capacity and therefore, less hydration water. Nevertheless, in these cases most of the water should be sorbed to the surface of the clay.

In montmorillonite and hectorite, the layer charge is due dominantly to Mg^{2+} for Al^{3+} substitution and Li^+ for Mg^{2+} substitution in the octahedral sheet, respectively. In beidellite, saponite, and vermiculite, however, the layer charge is derived primarily from substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet.

2. EXPERIMENTAL METHODS

2.1. NMR Methods

The ^2H NMR spectra were obtained using a Bruker MSL 300 Fourier-Transform NMR spectrometer ($B_0 = 7.05T$ at a frequency of 46.07 MHz).[†] The spectra were collected using a 10 mm broadband probe at temperatures from 189 to 299 ±1 K. For the water-dominated systems, a single pulse sequence of 3 μs (22.5°) was used and 1–16 scan(s) were collected for each sample. For the samples which had a small adsorbed D_2O component (clay/water > 1 g-clay/mL-D_2O), solid echo pulse sequences ($90_x - \tau - 90_y - \tau -$ Acquire) were utilized (Harris, 1986). Spin-lattice relaxation time measurements (T_1) were made using a solid echo inversion-recovery ($180_{\pm x}$ – Variable Delay – $90_{\pm x} - \tau - 90_y - \tau -$ Acquire) pulse sequence. For both types of experiments, the 90° pulses were 8.5–12 μs and the τ values ranged from 25 to 100 μs.

During variable-temperature NMR data collection, constant temperature was maintained by controlling a heating element in the probe. For experiments above room temperature, the heater regulated the drive gas N_2 temperature. For experiments below room temperature, the boil off from liquid N_2 was used to cool the sample, and a heater in the probe maintained the desired temperature. The ^2H chemical shifts are reported in Hz relative to 100% D_2O at 299 K.

2.2. Samples

The two samples chosen for this study are monomineralic Fe-poor 2:1 trioctahedral phyllosilicates: hectorite and saponite. The hectorite is from Hector, San Bernadino County, CA, USA (SHCa-1) with a structural formula of:

$$M^+_{0.72} \cdot [(Mg^{2+}_{5.31}Li^+_{0.69})(Si_{7.98}Al_{0.02})O_{20}F_{2.2}OH_{1.8}]$$

(Weiss et al., 1990a,b), and the saponite is from Ballarat, CA, USA (SapCa-1) with a structural formula of:

$$M^+_{0.98} \cdot [(Mg_{5.79}Al_{0.12}Fe_{0.07})(Si_{6.85}Al_{1.15})O_{20}OH_4]$$

(Callaway and McAtee, 1985). These minerals were obtained from the Clay Minerals Society. A <0.1 μm size fraction of each sample was obtained from the original material by centrifuging the dispersed sample.

2.3. Laboratory Preparation

The samples were prepared by suspending 0.75 g of clay in 100 mL of 0.1 M NaCl, NH_4Cl, or $CaCl_2$ solution of varying ratios (see Table 1). These suspensions were placed in sealed polyethylene bottles and shaken overnight in a waterbath at 60°C. The samples were then washed in doubly distilled/deionized water, centrifuged at 9000 rpm (13,200 g) for 30 min, and the supernatant decanted. This process was repeated at least 3×. The samples were then dried at 60°C overnight or until dry. For NMR analyses, two types of samples were prepared. (1) For water-dominated systems (clay/water = 0.0238 g-clay/mL-D_2O), a portion of clay was dried at 110°C and dispersed in the required amount of D_2O. (2) For clay-dominated systems (clay/water > 1 g-clay/mL-D_2O), a portion of clay was dried at 110°C and allowed to rehydrate in a 100% relative humidity D_2O atmosphere (closed desiccator with D_2O in the bottom) at 60°C for times from 5 min to 12 h.

3. RESULTS

3.1. Water-dominated Systems

Representative examples of ^2H NMR spectra for clay-water suspensions are shown in Fig. 1. Additional data on spin-lattice (T_1) relaxation rates and residual quadrupolar splitting (Δ) values are shown in Table 1. The figure depicts the spectra of a series of saponite clays exchanged in $CaCl_2$/NaCl solutions from 100% $CaCl_2$ to 100% NaCl. Within the series, the ^2H NMR spectrum for a $Ca^{2+}/Na^+ = 0$ (i.e., 100% Na^+) exhibits the largest ^2H quadrupolar splitting of 47.8 Hz. As Ca^{2+} is added to the system, the quadrupolar splitting decreases to 0 at 100% Ca. In saponite, as the Ca^{2+}/Na^+ ratio approaches ∞, the ^2H quadrupolar splitting approaches 0. However, a small asymmetry is observed in the spectrum of saponite for the Ca^{2+}/Na^+ ratio = 0. Spin-lattice relaxation values (T_1 = 400–430 ms) measured for these samples show no systematic variation and are within experimental error of the T_1 value expected for "free" or bulk water (Mantsch et al., 1978; Fripiat et al., 1984).

A series of ^2H NMR spectra of hectorite samples prepared analogously to the saponites (Fig. 1) are shown in Fig. 2. The

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[†] Reference to brand or firm name does not constitute an endorsement by the US Department of Agriculture over others of a similar nature not mentioned.

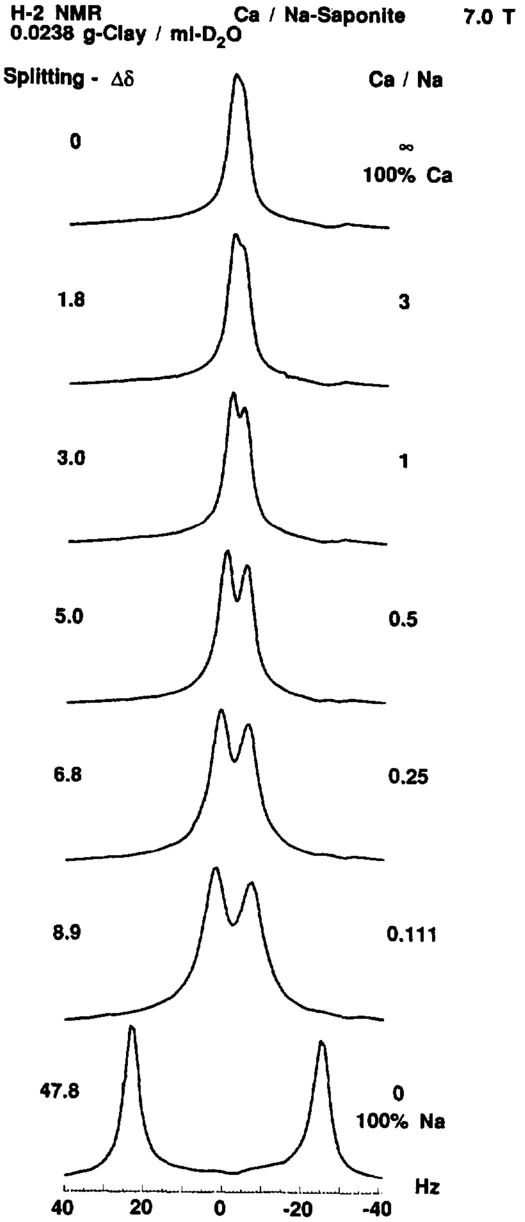

FIG. 1. A series of solution ^{2}H NMR spectra collected at 299 K of a saponite clay exchanged in $CaCl_2$/NaCl solutions from 100% $CaCl_2$ to 100% NaCl. In this figure and all others, the ^{2}H chemical shifts are reported in Hz relative to 100% D_2O at 299 K.

^{2}H NMR spectra of hectorite with a Ca^{2+}/Na^+ ratio = 0 (i.e., 100% Na^+) exhibits a splitting of 19.3 Hz. The widths (full width at half-maximum) of the left and right components of the doublet are 6.3 and 5.2 Hz, respectively. As with the previous saponite measurements, the spin-lattice relaxation values (T_1 = 400–430 ms) determined for these samples exhibit no systematic variation within the series, nor do these relaxation times deviate significantly from the T_1 of free water.

A series of solution ^{2}H NMR spectra (collected at 299 K) of a saponite clay exchanged in $CaCl_2/NH_4Cl$ solutions (ranging in concentration from 100% $CaCl_2$ to 100% NH_4Cl, Fig. 3) exhibit a very systematic diminution of splitting with increasing Ca^{2+}/NH_4^+ ratio. At Ca^{2+}/NH_4^+ = 0 (100% NH_4^+), the residual quadrupolar splitting is 54.4 Hz and the FWHM (Full Width at Half-Maximum) of each transition is 6–7 Hz. With an increase in the amount of Ca^{2+} to Ca^{2+}/NH_4^+ = 0.111, there is a corresponding decrease in the splitting to 29.6 Hz along with a broadening of the signals to 21–28 Hz, respectively. With further increases in Ca^{2+} ion concentration to Ca^{2+}/NH_4^+ = 0.25, the splitting diminishes to 14.2 Hz. At higher Ca^{2+}/NH_4^+ ratios, a single transition is observed with peak widths of the order of 12–13 Hz.

A series of ^{2}H NMR spectra of a saponite clay exchanged in NH_4Cl/NaCl solutions (from 100% NH_4Cl to 100% NaCl, Fig. 4) show small non-systematic variations in the splitting of the two transitions. However, systematic variation is evident in the width of the individual transitions. The ^{2}H spectrum of the 100% NaCl has the greatest quadrupolar splitting of 68 Hz and the narrowest widths for the individual transitions of 2.6 Hz. The splitting between the transitions in the spectrum for the sample with NH_4^+/Na^+ = 0.111 decreases slightly to 59 Hz and the widths of each transition broaden to ~5 Hz. The NH_4^+/Na^+ = 0.25 spectrum shows a small decrease in splitting to 58 Hz, but a much greater increase in width to ~7.8–8.5 Hz.

3.2. Clay-dominated Systems

The ^{2}H NMR spectrum of a sample with very little adsorbed water (Fig. 5) exemplifies the effect of decreasing water content. A hectorite clay with very little adsorbed water (final composition of this material was 12.81 g-clay/mL-D_2O) has four dominant transition maxima (Fig. 5). The two higher and more central maxima are at 2070 and −1840 Hz. The other two transitions are broader and located at 8170 and −8050 Hz. There are very evident singularities of the outer two transitions as seen in the spectrum. Variable-temperature NMR spectra were collected for a representative clay to more clearly understand the function of decreasing temperature on the motion of adsorbed water molecules. NMR spectra of a saponite clay exchanged in 0.1 M NaCl solution, rinsed of excess ions, dried at 110°C, and allowed to hydrate in a D_2O atmosphere for 30 min (4.05 g-clay/mL-D_2O, Fig. 6) were collected sequentially from 299 to 189 K. The splitting at 299 K is 11,400 Hz and increases only slightly to 12,500 Hz at 259 K. With further decreases in temperature to 229 K, the maxima have a greater splitting of 13,600 Hz. Furthermore, the intensity of the saddle between the maxima increases below 229 K, and progressively increases with decreasing temperature. The broadening of the signal can be ascribed due to loss of motion of the D_2O molecules with decreasing temperature.

A similar Na-exchanged hectorite sample (hydrated to 5.31 g-clay/mL-D_2O) was examined using variable-temperature NMR as a function of temperature from 299 to 189 K (Fig. 7). The spectra were collected sequentially from 299 to 189 K. The residual quadrupolar splitting at 299 K is 12,000 Hz and gradually increases to 15,000 Hz at 219 K. At 209 K, although the signal/noise ratio is poor, the last remnant of the doublet is observed. At 189 K, a broad peak is observed.

Table 1. Sample Names, Cation Ratios, Average T_1 Spin-lattice relaxation rates, ^{2}H chemical shifts[‡], and residual quadrupolar splitting for clay-water suspensions (clay/water=0.0238 g-clay/mL-D_2O) [Figs. 1-4].

Sample	$\frac{\mathrm{Ca}}{\mathrm{Na}}$	$\frac{\mathrm{Ca}}{(\mathrm{Ca}+\mathrm{Na})}$	T_1(ave.) 299K msec	δ - 299K Hz	δ - 299K Hz	$\Delta\delta$ - 299K Hz
Hect Ca/Na=0	0	0	421.6	5.84	-13.42	19.26
Hect Ca/Na=0.111	0.111	0.1	434.0	8.12	-16.65	24.77
Hect Ca/Na=0.25	0.25	0.2	424.7		-3.9	0
Hect Ca/Na=0.5	0.5	0.333	423.4	-1.24	-7.44	6.20
Hect Ca/Na=1	1	0.5	430.6		-4.75	0
Hect Ca/Na=3	3	0.75	406.4	-3.61	-9.0	5.39
Hect Ca/Na=∞	∞	1	397.4		-3.82	0
Sap Ca/Na=0	0	0	404.6	22.92	-24.86	47.78
Sap Ca/Na=0.111	0.111	0.1	405.8	2.22	-6.69	8.91
Sap Ca/Na=0.25	0.25	0.2	514.2	0.98	-5.78	6.76
Sap Ca/Na=0.5	0.5	0.333	478.9	-0.11	-5.15	5.04
Sap Ca/Na=1	1	0.5	421.2	-1.34	-4.31	2.97
Sap Ca/Na=3	3	0.75	448.9	-1.79	-3.59	1.80
Sap Ca/Na=∞	∞	1	437.4		-2.04	0
Sample	$\frac{\mathrm{NH_4}}{\mathrm{Na}}$	$\frac{\mathrm{NH_4}}{(\mathrm{NH_4}+\mathrm{Na})}$	T_1(ave.) 299K msec	δ - 299K Hz	δ - 299K Hz	$\Delta\delta$ - 299K Hz
Sap NH_4/Na=0	0	0	391.5	36.56	-32.22	68.78
Sap NH_4/Na=0.111	0.111	0.1	391.8	32.65	-27.30	59.95
Sap NH_4/Na=0.25	0.25	0.2	393.0	31.72	-26.94	58.66
Sap NH_4/Na=0.5	0.5	0.333	380.5	32.67	-27.66	60.33
Sap NH_4/Na=1	1	0.5	387.3	35.08	-23.35	58.43
Sap NH_4/Na=3	3	0.75	380.4	28.78	-15.93	44.71
Sap NH_4/Na=∞	∞	1	395.5	34.45	-23.64	58.09
Sample	$\frac{\mathrm{Ca}}{\mathrm{NH_4}}$	$\frac{\mathrm{Ca}}{(\mathrm{Ca}+\mathrm{NH_4})}$	T_1(ave.) 299K msec	δ - 299K Hz	δ - 299K Hz	$\Delta\delta$ - 299K Hz
Sap Ca/NH_4=0	0	0	416.9	28.23	-25.77	54.0
Sap Ca/NH_4=0.111	0.111	0.1	422.4	18.97	-9.92	28.89
Sap Ca/NH_4=0.25	0.25	0.2	444.0	9.93	-2.01	11.94
Sap Ca/NH_4=0.5	0.5	0.333	441.7		2.86	0
Sap Ca/NH_4=1	1	0.5	427.8		7.17	0
Sap Ca/NH_4=3	3	0.75	423.1		7.40	0
Sap Ca/NH_4=∞	∞	1	449.3		7.80	0

[‡] ^{2}H chemical shifts are referenced relative to a 100% D_2O solution at 299K as an external standard

4. DISCUSSION

4.1. Splitting Effects

The residual splittings observed are related to the amount of water associated with the particular clay. Our results affirm the idea that different clays have different amounts of bound water associated with them. These results attempt to quantify the amount of bound and free water molecules in these systems. In addition, variable-temperature NMR can document the changes in motion of the water molecules in clay-water systems with changes in temperature.

For clay-D_2O systems in a strong magnetic field, splitting of the $(0 \rightarrow 1)$ and $(-1 \rightarrow 0)$ transitions indicate that there is some local ordering of water molecules with respect to the clay surface (Grandjean and Laszlo, 1989a,b; Delville et al., 1991). The inability of water molecules to move freely due to their interactions with cations, as well as the clay, is manifested in a residual quadrupolar coupling (Δ), which is given by:

$$\Delta = \frac{3\mathrm{QCC}}{4I(2I-1)}[(3\cos^2\theta_{\mathrm{LD}} - 1)A], \qquad (1)$$

where I is the nuclear spin, QCC is the quadrupolar coupling constant, A is the residual anisotropy (with values between 1 and -1), and θ_{LD} is the angle between the static magnetic field (B_0) and the local order director vector of the oriented clay platelets (Halle and Wennerström, 1981). In the case for ^{2}H ($I = 1$), the residual splitting is expressed by $\Delta = {}^3\!/\!_4\mathrm{QCC}[(3\cos^2\theta_{\mathrm{LD}} - 1)A]$. Under the condition of slow exchange, the angle (θ_{LD}) is $\pi/2$, and $\Delta = {}^3\!/\!_4\mathrm{QCC}$ (see Grandjean and Laszlo, 1989a,b; Delville et al., 1991).

4.2. Cation Polarizability

In water-dominated systems, the residual quadrupolar splitting is small due to the presence of a large amount of free water (Figs. 1–4). In the saponite-($CaCl_2$/NaCl) exchanged clays, the largest splitting of 47.8 Hz is observed when $Ca^{2+}/Na^+ = 0$ (i.e., 100% Na^+). As the Ca^{2+} concentration is

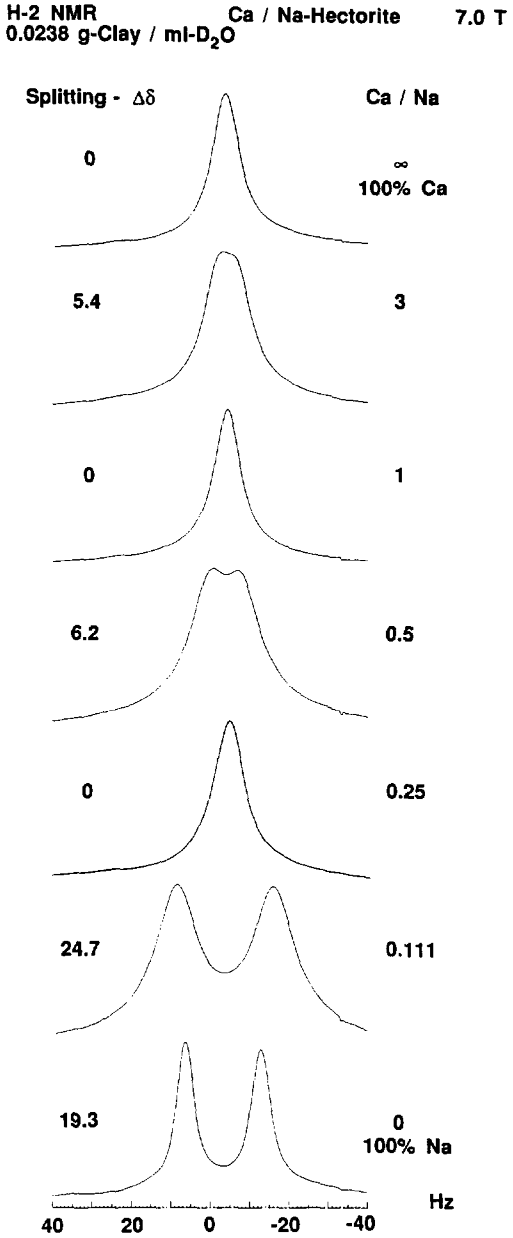

FIG. 2. A series of solution ^{2}H NMR spectra collected at 299 K of a hectorite clay exchanged in $CaCl_2$/NaCl solutions from 100% $CaCl_2$ to 100% NaCl.

increased to a ratio of (Ca^{2+}/Na^+) = 0.111, there is a marked decrease in the observed splitting to 8.9 Hz. The decreased splitting of the D_2O with increasing amounts of divalent ions has been succinctly explained by Grandjean and Laszlo (1989a). An increase in the number of divalent ions near the clay surface causes the bonding of the water molecules next to the clay to switch from rotation of water molecules around hydrogen bonds to rotation around the stronger divalent metal to oxygen bond. The authors keenly showed that for a Ca^{2+}/Na^+-exchanged montmorillonite, that the splitting approaches zero, and then is split again. They attribute these results to show that the rotation of water molecules around hydrogen bonds and those around the divalent metal have different signs.

The series of solution ^{2}H NMR spectra (collected at 299 K) of a saponite clay (exchanged in $CaCl_2/NH_4Cl$ solutions, Fig. 3) shows similar effects as the spectra of Ca^{2+}/Na^+-exchanged clays (Figs. 1, 2). A very systematic diminution of splitting occurs with increasing Ca^{2+}/NH_4^+ ratio. The difference between the set of Ca^{2+}/NH_4^+ samples and the Ca^{2+}/Na^+ samples is that the observed residual splitting diminishes more quickly for the Ca^{2+}/NH_4^+ samples. At Ca^{2+}/NH_4^+ = 0 (100% NH_4^+), the residual quadrupolar splitting is 54.4 Hz, but diminishes to 0 by Ca^{2+}/NH_4^+ = 0.5. The same reorientation of the bonding of the water molecules can also explain

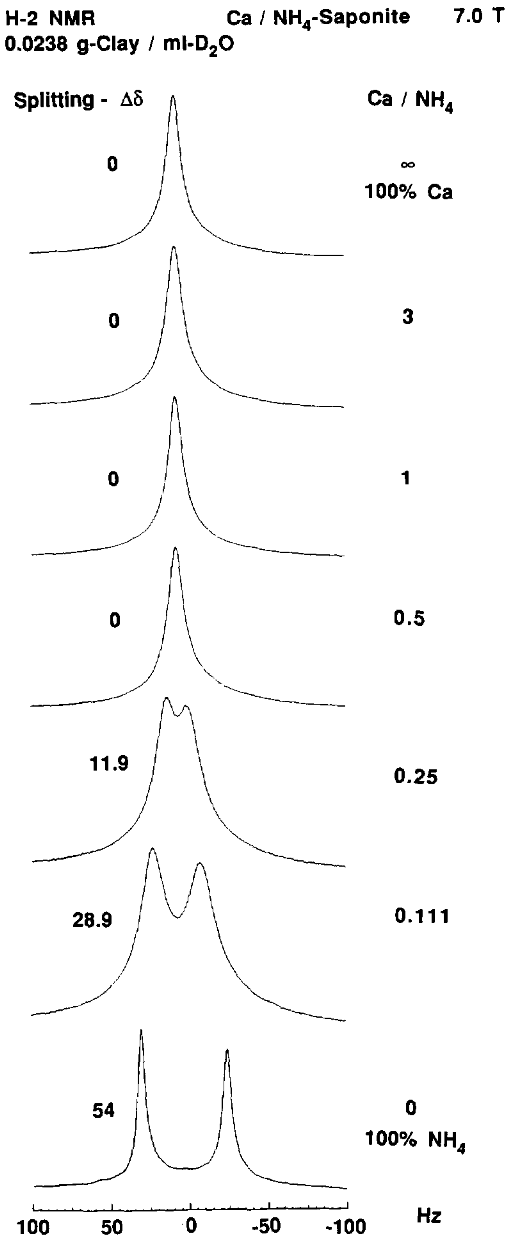

FIG. 3. A series of solution ^{2}H NMR spectra collected at 299 K of a saponite clay exchanged in $CaCl_2/NH_4Cl$ solutions from 100% $CaCl_2$ to 100% NH_4Cl.

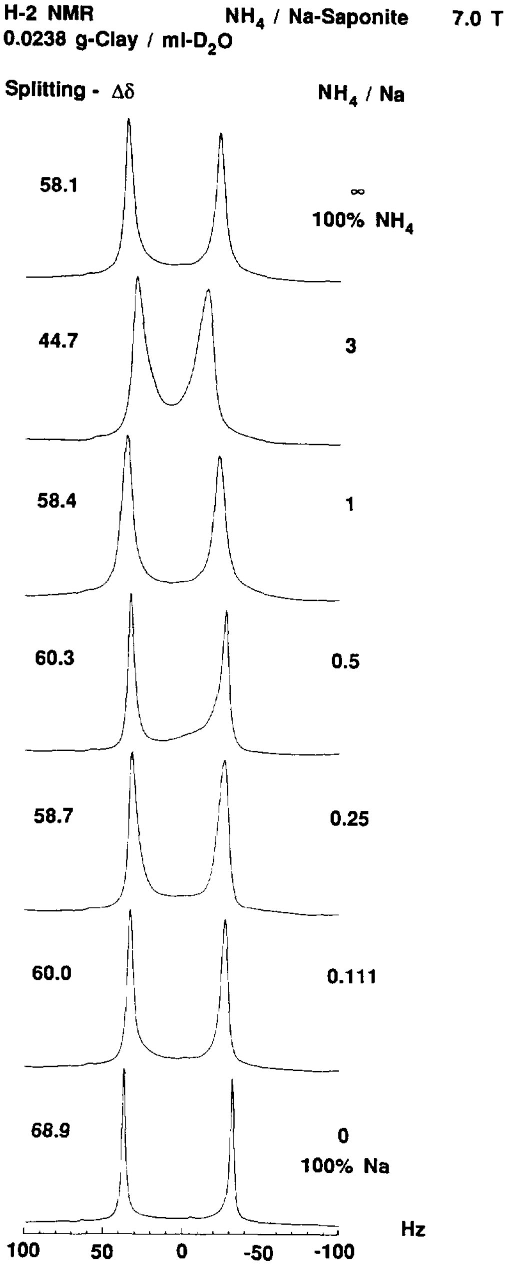

FIG. 4. A series of solution ^2H NMR spectra collected at 299 K of a saponite clay exchanged in NH_4Cl/NaCl solutions from 100% NH_4Cl to 100% NaCl.

these samples since both involve displacement of a univalent ion with a divalent ion. The increased broadening of the peaks probably occurs because of the heterogeneity of water sites present due to the two cations present on the clay.

The small variations in residual quadrupolar splitting observed for the series of ^2H NMR spectra of NH_4^+/Na^+ -exchanged saponite clay (Fig. 4) are related to the fact that both NH_4^+ and Na^+ ions are univalent and exhibit similar bonding properties with water molecules. The ^2H spectrum of the 100% NaCl-clay sample has the greatest splitting (68 Hz) between transitions and the narrowest widths of the individual transitions at 2.6 Hz. The small width of the transitions indicates that there is a very small range of orientations for water in this sample. Increasing the amount of NH_4^+ in this system increases the observed breadth because the range of orientations has increased in the mixed ion system.

4.3. Motional Averaging of Water

In these water-dominated system, water molecules are in fast exchange between "free" and bound water environments (Delville et al., 1991). The residual quadrupolar splitting (Δ) observed in the ^2H NMR spectra is given by:

$$\Delta = p_f \Delta_f + p_b \Delta_b, \qquad (2)$$

where p_f and p_b are the mole fraction of the "free" and bound water and Δ_f and Δ_b are the residual splitting of the "free" and bound components of the water (Delville et al., 1991).

An approximation for the number of water molecules that are "free" or bound in a given clay/D_2O can be calculated using Eqns. 1 and 2. Given that liquid water has a QCC of 0.23 MHz, the observed splitting of $\frac{3}{4} \cdot$QCC yields a $\Delta_b = 0.17$ MHz. Assuming a splitting of 1 Hz for "free" water and 48 Hz for the Na-exchanged saponite, we calculate that the mole fraction of water molecules bound to the clay (p_b) is approximately 3×10^{-4}. Furthermore, with decreasing residual quadrupolar splitting, the instantaneous fraction of water molecules interacting with the clay decreases. The presence of no splitting, however, does not preclude some binding of water molecules to the clay. The fact that the transition widths are broader for these systems than for liquid water indicates some motional averaging of water molecules between the clay and bulk water.

A similar effect is observed for the hectorite samples exchanged in $CaCl_2$/NaCl solutions (Fig. 2). However, the residual quadrupolar splitting is smaller than that observed for saponite under the same conditions. The splitting for the Na-exchanged saponite is 47.8 Hz compared to that for the Na-exchanged hectorite which is 19.3 Hz. This difference is observed for all samples run in this study. The observed splitting is related to the amount of water that is bound to the clay relative to the amount of free water. Our data indicate that

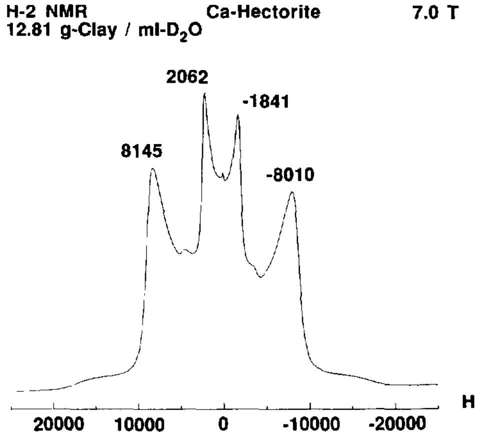

FIG. 5. A hectorite spectrum exchanged in a 0.1 M $CaCl_2$ solution, rinsed of excess ions, dried at 110°C and allowed to hydrate in a D_2O atmosphere. The clay/D_2O ratio is 12.81 g-clay/mL-D_2O.

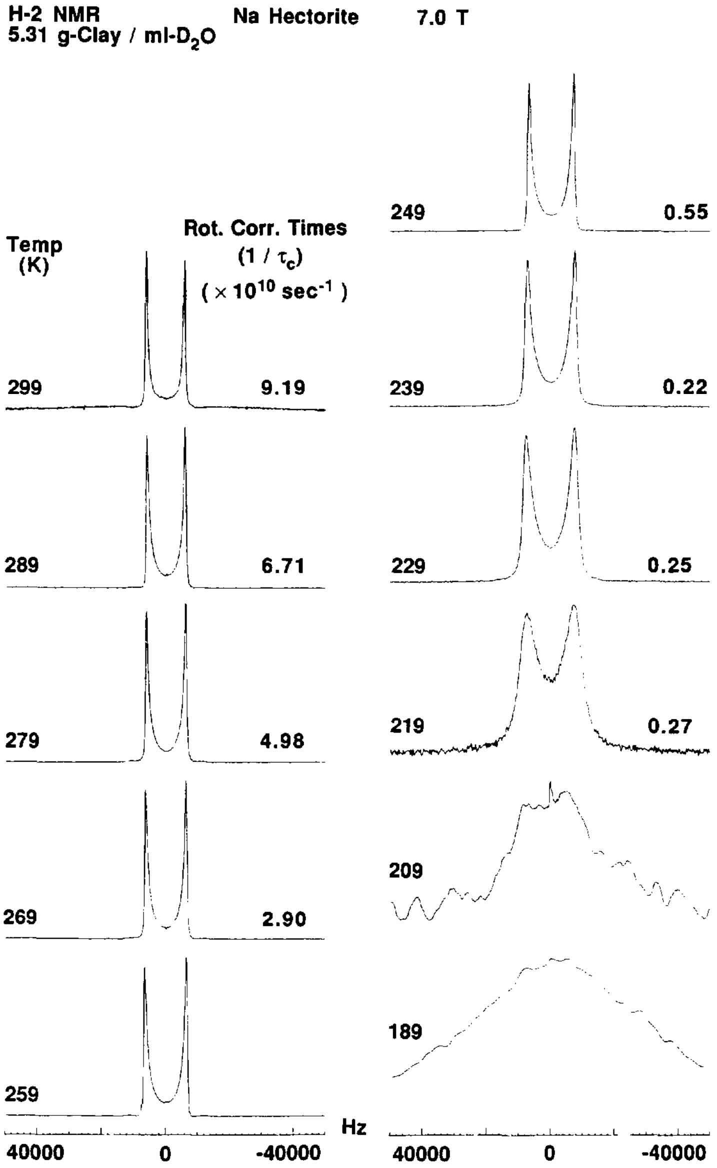

FIG. 6. A series of ^{2}H NMR spectra of a Na-exchanged saponite clay collected at temperatures ranging from 299 to 189 K. The sample was prepared as described in the samples section and allowing it to hydrate with D_2O to 4.05 g-clay/mL-D_2O. Rotational correlational ($1/\tau_c$) times calculated from the spin-lattice relaxation (T_1) times are indicated for most temperatures.

given the same clay to water ratio and the same cation, different clays have different amounts of bound water associated with them, i.e., saponite has more bound water than hectorite. This result is not totally unexpected because the layer charge on the saponite is greater than for the hectorite sample, there should be more interlayer cations present, and therefore, more hydration water. No determination can be made from these data that the location of the layer charge development (octahedrally derived for hectorite vs. tetrahedrally derived for saponite) has an effect on the ^{2}H NMR spectra.

4.4. Motional Nature of Water

In quadrupolar nuclides in the presence of water (i.e., when fast exchange is occurring), the spin-lattice relaxation rate (T_1^{-1}) of quadrupolar ^{2}H is defined by:

$$T_1^{-1} = \tfrac{3}{10}\pi^2 \frac{2I+3}{I^2(2I-1)} \mathrm{QCC}^2\left(1+\frac{\eta^2}{3}\right)\tau_c, \qquad (3)$$

where I is the nuclear spin, QCC is the quadrupolar coupling constant, η is the asymmetry parameter, and τ_c is the correlation time (Grandjean and Laszlo, 1989b). For ^{2}H, $T_1^{-1} = \tfrac{3}{2}\pi^2\mathrm{QCC}^2\left(1+\frac{\eta^2}{3}\right)\tau_c$. For ^{2}H in these systems, a limiting value for the correlation time (τ_c) of τ_c of 2.93×10^{-12} s was given relative to 100% D_2O with a T_1 of 0.436 s and a QCC of 230 kHz (Mantsch et al., 1978; Fripiat et al., 1984). Binding or interaction of water to molecules has been associated with a concomitant decrease in the measured spin-lattice relaxation rate (Mantsch et al., 1978). If τ_c values for ^{2}H of D_2O in clay-water mixtures are less than that for bulk D_2O,

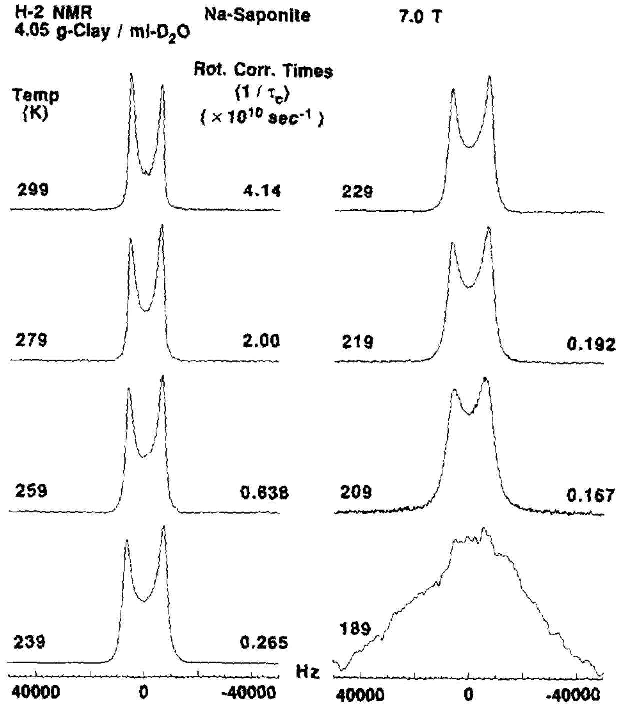

FIG. 7. A series of ^{2}H NMR spectra of a Na-exchanged hectorite clay collected at temperatures from 299 K to 189 K. The sample was prepared as described in the samples section and allowing it to hydrate with D_2O to 5.31 g-clay/mL-D_2O. Rotational correlational ($1/\tau_c$) times calculated from the spin-lattice relaxation (T_1) times are indicated for given temperatures.

the spin-lattice relaxation rate (T_1^{-1}) for these systems must be less than that for free water (and the spin-lattice relaxation time, T_1, would be greater than for free water). Changes in rotational correlation have a large effect on the observed NMR spectra (Fig. 8). Although this figure (from Stockton et al., 1976) describes CD (carbon-deuterium bond) rotation correlation time, τ_c ($= \tau_r$), dependence for vesicles in lipid systems, we can ascribe similar effects to OD (oxygen-deuterium bond) systems such as in clay-water systems. At very low τ_c values (e.g., (10^{-1} s·rad^{-1}), broad Pake powder patterns are observed, with residual quadrupolar splitting (D_q). With increasing τ_c there is a progressive broadening of the maxima and a collapse of the Pake pattern. At the shortest τ_c, there is no Pake pattern, only a single narrow line. Using this example, one sees that as the concentration of divalent cations is increased, there is a decrease in τ_c, and a collapse of the residual splitting. Because the amount of residual splitting is so small in these water-dominated/clay systems (<100 Hz), only small changes in τ_c could cause the collapse of the splitting as observed. For these water-dominated/clay systems, the spin-lattice relaxation values ($T_1 = 400$ to 430 msec) measured are all very similar because the spectra are dominated by the large amount of bulk water with shorter rotational correlation time, relative to the water that sees the clay-cation system with longer τ_c.

4.5. Clay-dominated Systems

In the clay-dominated systems, much less exchange occurs between bulk or free water and the water hydrating the cations and there is less motional averaging of chemical shifts, the rotational correlation times decrease (Fig. 7), and the residual quadrupolar splittings increase as the clay/water ratio increases (Fig. 5). For instance, the ^{2}H spectrum of Ca-exchanged hectorite (12.81 g-clay/mL-D_2O; Fig. 5) has two different water environments, one with 80% of the signal and a QCC of 23 kHz and another with 20% of the signal and a QCC of 6 kHz. Because decreased residual quadrupolar splitting indicates that a greater fraction of the water is absorbed on the clay, the widely different quadrupolar splittings indicate that there is an unequal distribution of water in this sample.

4.6. Slowing Down the Motion of the Water Molecules

4.6.1. Saponite

The variable-temperature NMR spectra for the Na-exchanged saponite (hydrated to 4.05 g-clay/mL-D_2O, Fig. 6) show little change in the splitting observed in the temperature region from 299 to 259 K. With further decreases in temperature to 239 and 229 K, the maxima have a larger splitting of 13,700 and 13,600 Hz, respectively. Furthermore, the intensity of the saddle between the maxima increases below 249 K and progressively increases with successive decreases in temperature. These changes can be explained by the fact that at these low water contents, the freezing point of D_2O is depressed to 259 or 249 K. As the water on the clay freezes, the range of orientations in which the water molecules are found increases and there is a broadening of the individual transitions.

4.6.2. Hectorite

The Na-exchanged hectorite clay (hydrated to 5.31 g-clay/mL-D_2O, Fig. 7) shows small increases in residual quadrupolar splitting with small decreases in temperature in the range from 299 to 229 K. At temperatures below 219 K, the individual transitions broaden, causing an increased saddle between the two transitions. At 209 K, the signal/noise ratio is poor, but a small residual of the doublet can still be observed. With a further decrease in temperature to 189 K, the presence of an amorphous single peak indicates that the sample is frozen.

4.7. Rotational Correlation Times for Water Molecules

4.7.1. Saponite

The spin-lattice relaxation times (T_1's) for this Na-exchanged saponite sample decrease with decreasing temperature from 52.9 ms at 299 K to 3.47 ms at 239 K. Further decreases in temperatures do not seem to have much effect on T_1, and the T_1 values plateau out at 2 ms. Thus, the inverse of the resultant rotational correlation times ($1/\tau_c$'s) also decrease with decreasing temperature from 4.14×10^{10} s^{-1} at 299 K to 0.265×10^{10} s^{-1} at 239 K, giving an activation energy (E_a) for water molecule rotation (Fig. 9) of 27.2 kJ·mole^{-1} (or 6.5 kcal·mole^{-1}).

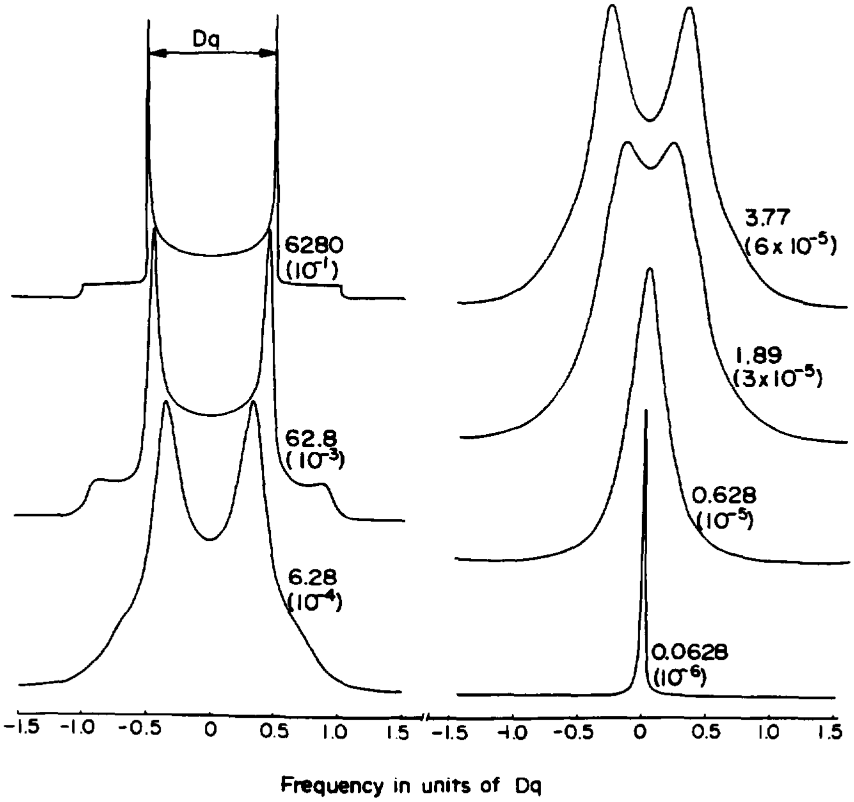

FIG. 8. An illustrative example of the effect of rotational motion on ^{2}H NMR spectra. These spectra are simulated ^{2}H NMR spectra for CD fragments with residual quadrupolar splitting (D_q) of 10 kHz. The numbers beside the spectra are $2\pi D_q \tau_r$, which relates the rotational correlation time (τ_r, number in parentheses) and residual splitting (Stockton et al., 1976).

4.7.2. Hectorite

The spin-lattice relaxation times (T_1's) for the Na-exchanged hectorite sample decrease with decreasing temperature from 117.3 ms at 299 K to 2.9 ms at 239 K. Further decreases in temperatures do not seem to have much effect on T_1, and the T_1 values plateau out at 2 ms. Furthermore, the resultant rotational correlation times ($1/\tau_c$'s) also decrease with decreasing temperature from 9.19×10^{10} s^{-1} at 299 K to 0.22×10^{10} s^{-1} at 239 K, giving an activation energy (E_a) for water molecule rotation (Fig. 9) of 37.8 kJ·mole^{-1} (or 9.0 kcal·mole^{-1}). These calculated activation energies of rotation for water of hydration for both the saponite and hectorite samples are similar to those of a Na-exchanged vermiculite sample (8.5 kcal·mole^{-1}, Giese and Fripiat, 1979). These results might indicate that water is more influenced by the cation than by the clay structure itself, but more data on different clays and using other cations is needed to substantiate these results.

4.8. Future Work

Other candidates for future research into the interaction of phyllosilicates with water include montmorillonites, beidellites, and vermiculites. These minerals have widely different cation exchange capacities and have charge development both near and far to the interlayer. These studies would be useful in comparison to the IR work of Sposito et al. (1983), Fu et al. (1990), and Johnston et al. (1992).

Other cations to be investigated include the univalent Cs cation and the small univalent Li cations. Furthermore, clay/water ratios intermediate to those investigated here should be investigated, and may yield information to explain the nonsystematic behavior of the ^{2}H splittings for the Ca/Na-exchanged hectorite samples. More work similar to Grandjean and Laszlo (1989a) is needed to determine for different clays, cations, and water contents the changes in bonding that occur in these systems. Investigations of clays with extremely low water contents may yield new information on different bonding sites which are masked in the dilute clay suspensions.

5. CONCLUSIONS

The ^{2}H quadrupolar splitting and spin-lattice relaxation times (T_1) are related to the ratio of clay to adsorbed water in the system.

In water-dominated systems (clay/water ratio $\leqslant 1$), motional averaging between water hydrating the cations and the "free" or bulk water occurs. In these systems, the spin-lattice relaxation (T_1) is dominated by the relaxation of the "free" water and has values close to that for a 100% D_2O solution (0.436 s) and the rotational correlation time (τ_c) approaches that of free water of 2.93×10^{-12} s. For the clay systems in this study with clay/water = 0.0238 g-clay/mL-D_2O, the

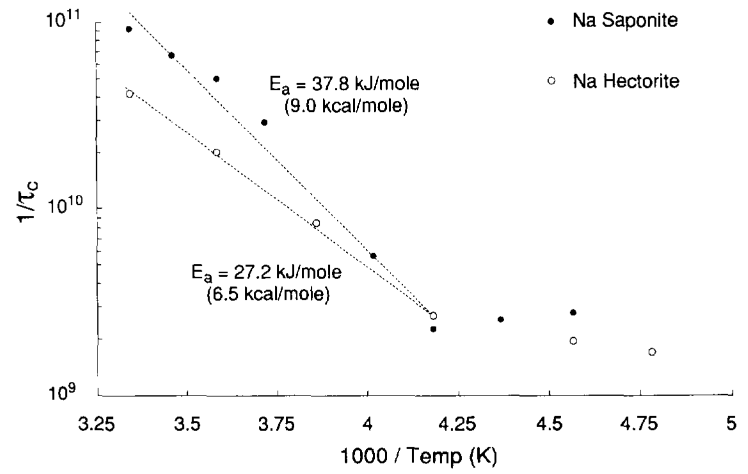

FIG. 9. Plot of $1/\tau_c$ vs. 1000/Temperature (K) for the Na-exchanged hectorite and saponite clay samples shown in Figs. 6 and 7.

quadrupolar splittings are of the order of <100 Hz, and the number of water molecules that are bound to clay are of the order of 1 in 10^3.

In clay-dominated systems (clay/water ratio > 1), less motional averaging occurs, rotational correlation times are slower and greater residual quadrupolar splittings are observed. Increased residual quadrupolar splittings are observed with increasing clay/water ratios. For a Na-exchanged saponite (4.05 g-clay/mL-D_2O), splittings are of the order of 11 kHz. An activation energy of 27.2 kJ·mole^{-1} (6.5 kcal·mole^{-1}) for the rotation of water molecules adsorbed onto Na-exchanged saponite was calculated from spin-lattice relaxation (T_1) measurements. For a Na-exchanged hectorite sample (5.31 g-clay/mL-D_2O), the quadrupolar splittings are of the order of 12 kHz, and the activation energy for the rotation of water molecules is 37.8 kJ·mole^{-1} (or 9.0 kcal·mole^{-1}).

The similarity of the calculated activation energies for both Na-exchanged hectorite and saponite clays, as well as the reported value for Na-exchanged vermiculite (8.5 kcal·mole^{-1}, Giese and Fripiat, 1979) supports the notion that the water is more influenced by the cation than by the particular clay.

For all clays in this study, there is a systematic decrease in ^{2}H splitting with increasing amounts of Ca^{2+} relative to either Na^+ or NH_4^+. This behavior can be attributed to changes in the orientation of the water molecules in contact with the clay tactoid as described in Grandjean and Laszlo (1989a).

Acknowledgments—We thank Craig M. Jacobs for his technical assistance and Peter Irwin for helpful discussions. We also thank N. Skipper and two anonymous reviewers for their comments.

Editorial handling: G. Sposito

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