DEUTERIUM NUCLEAR MAGNETIC RESONANCE STUDIES OF WATER MOLECULES RESTRAINED BY THEIR PROXIMITY TO A CLAY SURFACE

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Abstract—Observation of quadrupolar splittings for ^2H and ^{17}O nuclei from D_2O solvent molecules in suspensions of the Ecca Gum BP bentonite points unambiguously to the ordering of water molecules with respect to a static magnetic field. The application of the magnetic field apparently orients the clay platelets as tactoids. Some water molecules adhere to the platelets and are oriented. The magnitude of the quadrupolar splitting depends strongly on the nature of the interstitial cations. The sign of the splitting changes as the ratio of divalent to monovalent cation increases, reflecting a switch in the microdynamics of water molecules next to the plates. With the entry of divalent cations, the clay becomes more cohesive due to the vertical electrostatic attraction of the counterions to the charged plates. More of these hydrated divalent ions compared with monovalent ions condense onto the charged sheet, thereby increasing metal coordination to those water molecules in contact with the clay surface. The dominant reorientation mode of the water molecules switches from rotation of water molecules around hydrogen bonds to the charged sheets to rotation around the electrostatic bond to the divalent metal cation. The effect is spectacular and important in understanding the chemical properties of cation-exchanged montmorillonites.

Key Words—Nuclear magnetic resonance, Orientation, Quadrupolar splitting, Smectite, Surface acidity, Water.

INTRODUCTION

The present study examines the non-zero time average features in the immediate neighborhood of a charged clay surface. Such a region can be defined in a number of ways, with partial overlap between the various definitions: (1) by the range of van der Waals forces emanating from surface atoms; (2) by the diameter of the solvated counterions condensed to the surface; (3) as the region where the ionic strength is much higher, due to such condensation (electric double-layer); and (4) by the order of magnitude of the mean free path of molecules colliding with the surface. Whatever the definition, this region is of paramount interest in studying intercalation applications and activation in the heterogeneous catalysis of organic molecules (Laszlo, 1987).

Both neutral molecules and counterions are constrained by the presence, a few Ångstroms away, of a planar charged surface. Translations are unimpeded tangentially to the surface and occur with reflection radially to the surface. A rotating dipole, such as that of a water molecule, may be expected to point its positive end towards the negatively changed aluminosilicate sheet. To monitor such local orderings quadrupolar splittings of the deuterium (^2H) nuclear magnetic resonance may be measured for deuterons in water molecules (Wong and Hakala, 1985; Hakala and Wong, 1986). Such splittings can be detected, if water molecules reside in non-isotropic environments. Because water molecules migrate from the vicinity of clay plate-lets to the bulk, and because deuterons can hop between water molecules of these two kinds, only a time-averaged picture can be observed. Nevertheless, it yields valuable information about the solvent layer(s) partly immobilized at the interface with the clay mineral.

The present study thus examines the structure and microdynamics of water adsorbed at the clay interface. This problem is important, if only for these two reasons: (1) it is highly relevant in explaining the very high surface acidities of many clays; and (2) water structuring at the interface is also important to the reactivity of the clay and offers a model for the adsorption of other neutrals, such as alcohols.

THEORY

The spin quantum number I for the deuterium nucleus is unity. Accordingly, the ^2H nucleus assumes $2I + 1 =$ three spin states in a static B_0 magnetic field: $+1$, 0, and -1. The two allowed nuclear magnetic resonance transitions are the ($+1 \rightarrow 0$) and the ($0 \rightarrow -1$) transitions. For an isolated nucleus they are degenerate. They become non-degenerate in the presence of a non-vanishing quadrupolar interaction $\chi = (e^2q \cdot Q/\hbar)$, where q is the electrostatic field gradient $\left(q = \dfrac{\partial^2 V}{\partial z^2}\right)$ at the nucleus, and Q is the quadrupolar moment of the nucleus, a constant.

The quadrupolar coupling constant χ for deuterons is of the order of magnitude of 200 kHz. This provides the necessary leverage. A quadrupolar splitting of 5 Hz
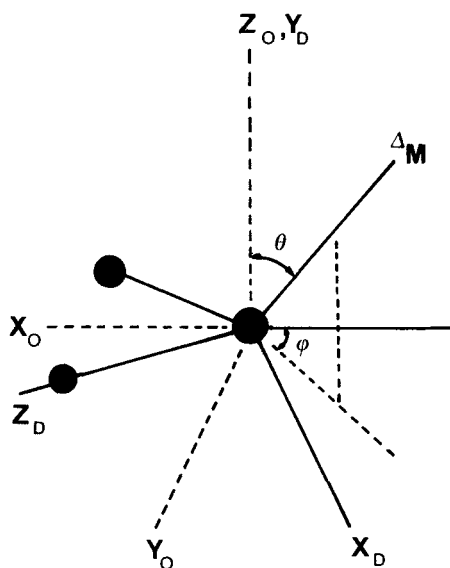
Figure 1. Principal axes for the ^2H and ^{17}O electrostatic field gradient tensors. The notation is that of Halle and Wennerstrøm (1981). The local director is denoted Δ_M.

is easily detected and measured. Therefore, even if only a minute fraction, e.g., one water molecule out of 10,000, of solvent molecules are associated with the clay surface (and "tagged" in some way by this association), this diminutive quantity will be detected in an unambiguous manner by the presence of a doublet for the deuteron resonance.

The question then arises, how can water molecules become "tagged" from their proximity to the charged sheet of a layer silicate differently from gallery (interlamellar) and from bulk water molecules. From the point of view of the quadrupolar interaction, they become "tagged" because of a significantly greater electrostatic field gradient. From the point of view of their mobility, they become "tagged" because of a slowdown of their reorientational motion when they become trapped in the high ionic atmosphere at the interface. For the background to these assertions, the reader is referred to McConnell (1958), Swift and Connick (1962), and Lindman and Forsén (1976).

Distinct $(0, +1)$ and $(-1, 0)$ ^2H transitions must be caused by partial alignment of the molecular axes for a given water molecule in the direction of the B_0 static magnetic field in which the sample is immersed for the nuclear magnetic resonance experiment. This ordering occurs as follows: Parallel stacks of clay platelets orient themselves collectively with respect to the B_0 field. The electrically charged sheets most probably interact strongly with the applied magnetic field. Placing the electrical distributions in a magnetic field locally generates electric currents that have magnetic dipoles associated with them, as a matter of course. The interaction of these magnetic dipoles with the magnetic

induction field B_0 orients the dipoles and, hence, the clay platelets with respect to B_0. This diamagnetic interaction is very strongly anisotropic, differing markedly in magnitude if the static magnetic field is aligned with the plane or perpendicular to it. A good analogy is a nematic liquid crystal; the elongated molecules align themselves parallel to one another and with their long axes parallel to the applied B_0 magnetic field. Water molecules do not move totally at random with respect to the walls of the aluminosilicate boxes encasing them. They "stick" to a certain extent to these walls. Several physical interactions are responsible. The electric dipole of a water molecule orients toward the electric charges on the polyanionic sheet. Water molecules also orient with respect to the platelets because they coordinate a cation condensed near the negatively charged separation plane, because they coordinate an anion repelled by it, or because they are part of a hydrogen-bonded network containing some strongly immobilized water molecules. For a single water molecule, coexistence of these various effects is likely; it may be hydrogen-bonded to other water molecules, it may also coordinate an ion, and it may undergo another strong interaction of the charge-dipole type with the surface charge density on the aluminosilicate sheet. Based on this broad picture and the theoretical analysis of Halle and Wennerstrøm (1981), Grandjean and Laszlo (1989a) applied corresponding equations to clay systems.

The following interpretations of the residual splittings have been formulated using the model of Halle and Wennerstrøm (1981), the seminal work in this field. Interaction of the water molecules or of the sodium counterions with the clay surface puts a constraint on their reorientation. It can translate into a residual splitting if it is made anisotropic—e.g., by preferred orientation of this wall (see above)—and if molecular mobility does not make the quadrupolar hamiltonian vanishingly small. Halle and Wennerstrøm (1981) solved the problem explicitly for water molecules (Figure 1).

The residual coupling Δ is given by:

$$\Delta = \frac{3\chi}{4I(2I-1)} \langle (3\cos^2\theta_{LD} - 1)A \rangle, \qquad (1)$$

where χ is the quadrupolar coupling constant and θ_{LD} is the angle between the static B_0 magnetic field and the local order director of the oriented aluminosilicate sheets, perpendicular to their parallel surfaces. We assume that this angle θ_{LD} remains constant, i.e., that its modulation is slow with respect to the residual quadrupolar interaction. The residual anisotropy A is expressed as a function of the Saupe ordering tensor main components S and of the Euler angles describing the orientation of a water molecule with respect to the local director (surface) as:

$$A(^2H) = (3 \cos^2\beta - 1 + \eta \sin^2\beta)S_0^2/2$$
$$- \{[3 \sin^2\beta + \eta(\cos^2\beta + 1)]S_2^2\}/2\sqrt{6} \quad (2)$$

and the residual anisotropy for the quadrupolar ^{17}O nucleus of water is:

$$A(^{17}O) = -(1 - \eta)S_0^2/2 + (3 + \eta)S_2^2/2\sqrt{6} \quad (3)$$

where β is one of the Euler angles relating the principal axes of the electric field gradient tensor of the nucleus to the Saupe ordering tensor of the molecule, the diagonal elements of which are denoted as S_{11}, S_{22}, and S_{33}. S_0^2 and S_2^2 are defined as $S_0^2 = S_{33}$ and $S_2^2 = 2(S_{11} - S_{22})/\sqrt{6}$, and η is the asymmetry parameter with values for ^2H and ^{17}O in water of 0.11 and 0.93 (Halle and Wennerstrøm, 1981) (Edmonds and Mackay, 1975; Edmonds and Zussman, 1972), respectively. Eqs. (1) and (2) correspond to the same choice of Euler angles as Halle and Wennerstrøm's. Accordingly, the angle β is equal to one-half the molecular DOD angle in heavy water. The values of the S_0^2 and S_2^2 parameters in Eqs. (1) and (2) depend on the mode of reorientation of water molecules, which may be assumed to occur predominantly around one of the molecular axes. Water molecules may occur in the bulk, in which case they reorient freely and isotropically around their three inertial axes.

In this discussion the quadrupolar coupling constant χ for deuterium in D_2O molecules (and likewise for oxygen-17) is assumed to be not very different from that measured in ice (Edmonds and Mackay, 1975; Edmonds and Zussman, 1972). Edmonds Mackay (1975) and Edwards and Zussman (1972) reported that χ values do not depend strongly on structure, but are affected more significantly by hydrogen bonding. Because negatively charged oxygens and hydroxyl silanol groups on the surface are the acceptor sites, similar electronic distributions should exist for the O–D bonds next to the clay surface and in ice.

Water molecules held in an attractive interaction display interesting effects. If a water molecule coordinates a positive charge via one of its lone pairs on oxygen, because of the electrostatic bond between water and the cation, a preferred mode of reorientation is internal rotation around the oxygen-cation axis. This axis may be that of the lone pair or it may be colinear with the molecular electric dipole. The lone pair model is characterized by angles θ and ϕ, in a standard notation (Chachaty and Quaegebeur, 1984), about 35° and 0°, respectively.

Another limiting reorientational mode occurs for water molecules held by a hydrogen bond to an anionic center. The water molecules tend to rotate around an axis connecting the O–D bond (in heavy water), the negative charge serving as hydrogen-bond acceptor. The lowest energy configuration for three atoms A–H . . . B engaged in a hydrogen bond is linear (Huheey, 1983; Hamilton, 1962). For such water the molecules reori-
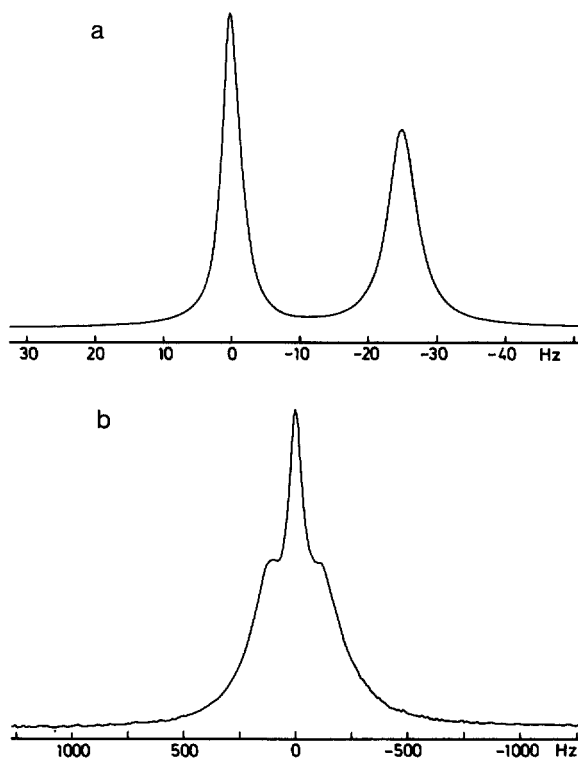

Figure 2.   Typical deuterium (a) and oxygen-17 (b) magnetic resonance spectra of Na$^+$-exchanged Ecca Gum BP bentonite (320 K, clay content 34 mg/ml).

ented by rotation around the O–D axis, the angles θ and ϕ are 90° and 128°, respectively.

This simple dichotomy is easily translated in terms of Eq. (3). The ^{17}O residual anisotropy consists of two terms. The first, that in S_0^2, is vanishingly small inasmuch as the asymmetry parameter η is close to unity (Halle and Wennerstrøm, 1981). The second term is proportional to S_2^2, which, in turn, has values of -0.3 ("hydrogen bond" reorientation) or $+0.4$ ("lone pair" reorientation). Thus, oxygen-17 splittings of either sign should be expected depending upon the preferred mode of reorientation. A similar effect is to be expected for the deuterium splittings.

EXPERIMENTAL

The sample examined was Ecca Gum BP (English China Clay, St. Austell, Cornwall) stirred in suspension into a metal chloride solution overnight. Before ion exchange, the composition of this bentonite was: Al_2O_3, 17.32; CaO, 0.48; MgO, 2.10; Fe_2O_3, 3.76; Na_2O, 3.13; K_2O, 0.07. The suspension was then centrifuged and washed until excess chloride was eliminated (as tested by reaction of the filtrate with silver nitrate). The ion-exchanged clay was then dried at 60°C, ground into a powder, and stored overnight at 100°C. The cation-exchange capacity of the exchanged bentonite was 95 ± 3 meq/100 g. The clay suspensions were saturated

Table 1. Deuterium quadrupolar splittings $\Delta\delta$, as a function of the Ca:Na ionic ratio.[1]

Sample[2]	Ca^{2+}/Na^+	$\Delta\delta$ (Hz)
1	0.002	$+16.3 \pm 0.1$
2	0.020	$+14.4$
3	0.0653	-2.2
4	0.1266	-14.6
5	0.1642	-19.4
6	0.2080	-20.6
7	0.4638	-22.2

[1] At 299 K, for clay suspensions (0.0238 g/ml D_2O).
[2] Ion-exchanged Ecca Gum BP bentonite.

Table 2. Deuterium quadrupolar splittings, $\Delta\delta$, as a function of the Mg:Na ionic ratio.[1]

Sample[2]	Mg^{2+}/Na^+	$\Delta\delta$ (Hz)
1	0	$+16.3 \pm 0.1$
8	0.0206	$+12.7$
9	0.0422	$+7.5$
10	0.1464	0
11	0.1987	0
12	0.2728	0

[1] At 299 K, for clay suspensions (0.0238 g/ml D_2O).
[2] Ion-exchanged Ecca Gum BP bentonite.

with NH_4Ac (pH = 7) and centrifuged after ~16 hr. Analysis of the exchangeable cations was made by atomic absorption on a 603 Perkin Elmer apparatus (accuracy ± 3%). The appropriate amount of the clay was stirred in suspension in D_2O (99.8 atom % D, Merck) for 24 hr prior to recording the spectra.

Nuclear magnetic resonance spectra were recorded with a Bruker AM 300WB spectrometer (B_0 = 7.05 T) at nominal frequencies of (MHz) 46.07 (^2H) and 40.69 (^{17}O). In typical ^2H experiments, 16 transients were acquired in 8 K points, with a spectral width of 1000 Hz and were transformed with 32 K points (digital resolution 0.06 Hz). The $\pi/2$ pulse width was 30 μs. For ^{17}O at natural abundance, 10 K scans were accumulated in 2 K points with a spectral width of 16 kHz and were transformed with 8 K points (digital resolution 3.9 Hz). The $\pi/2$ pulse width was 23 μs.

Deconvolution procedures, assuming all Lorentzian lineshapes (Grandjean and Laszlo, 1989b), were used for all ^{17}O spectra and for a few ^2H spectra if the doublet was not sufficiently resolved. The uncertainty in the determination of the line splitting was about 0.2 Hz for ^2H and about 5 Hz for ^{17}O. The uncertainty was rather large in the latter experiments because of the width of the oxygen-17 signals. The temperature was accurate to ±0.5°C. Longitudinal relaxation times were measured with the inversion-recovery sequence 180°-t-90°, followed by a non-linear regression on the exponential curve, using between 13 and 16 data points.

RESULTS

^2H splittings are listed in Tables 1 and 2 for various ratios of exchangeable cations. As shown in Table 1, the sign of the quadrupolar splitting changed from positive to negative as the proportion of divalent calcium increased. This observation is unambiguous, and despite the fact that the two components of the ^2H doublet shared identical longitudinal relaxation times T_1, the widths differed slightly. The $\Delta\delta$ splitting was arbitrarily set as positive if the broader resonance was at higher field (lower frequency).

Hakala and Wong (1986) recently reported a related observation from a study of the orientation of water molecules within uniaxial lyotropic mesophases. If Mg

was the divalent cation coexisting with Na in the interlamellar phase, the quadrupolar ^2H splitting also decreased if the ratio of divalent to univalent ion increased and became zero, but did not go to significantly negative values (Table 2). The ratio of the ^{17}O to the ^2H quadrupolar splitting (Table 3) changed from a high of 5.0 to a low of zero—a remarkable finding. In earlier investigations of water ordering by liquid crystalline solutes (Wong and Hakala, 1985; Hakala and Wong, 1986), this ratio was invariant at about 6. In a recent paper (Guo and Wong, 1987) values as low as 2.1 were reported.

DISCUSSION

The key results to be explained and discussed are the change in sign of the residual anisotropies (Tables 1 and 2) and the attendant variations of the $^{17}O/^2H$ ratio. These data point unambiguously to a profound structural change in the distribution of solvent molecules at the interface, depending on the nature of the exchangeable interlamellar cations.

The logical link to be first established connects the observed ^2H and ^{17}O splittings with the *populations* of water molecules squeezed between the condensed counterions and the charged aluminosilicate sheet. First, water molecules in the clay suspensions studied here are assumed to have retained to first approximation a constant O–D bond length, so that changes in the quadrupolar splitting were due predominantly to other factors. Second, a negligible impact of prototropic exchange of deuterons was assumed between water molecules on the quadrupolar splittings. Were such an effect significant, the ^2H splittings would have been

Table 3. Ratio of the ^{17}O to the deuterium quadrupolar splittings.[1]

Sample[2]	$\Delta\delta(^{17}O)/\Delta\delta(^2H)$
1	5.0
2	5.0
4	5.0
5	±3
7	±0

[1] At 320 K.
[2] Na-exchanged Ecca Gum BP bentonite.

vanishingly small, but ^{17}O splittings would not have been affected (even in DO^- the oxygen has a non-spherical environment). This would have led to $^{17}O/^2H$ ratios $\gg 6$, contrary to observation (Table 3).

Third, for gels such as those studied here the water content is high compared to the clay and, thus, to interlamellar water. Grandjean and Laszlo (1989b) showed that water molecules exchange rapidly between the bulk and the interface of the platelets. No quadrupolar splitting can exist for isotropic pure water, in the bulk. Thus, the splittings recorded in Tables 1 and 2 are directly proportional to the population of water molecules at the interface (Grandjean and Laszlo, 1988, 1989b).

The data of Tables 1–3 can be interpreted unambiguously. Because the residual splittings changed sign, a switch in the predominant reorientational mode of water molecules must have occurred. Logically this could have taken place if (and only if) water molecules were being coordinated *simultaneously* to anionic and to cationic sites. The present data resulted only from water molecules sandwiched between interstitial cations and the negatively charged density on the aluminosilicate sheet. The NMR observations reported here directly confirm the atmospheric condensation theory; i.e., fully hydrated cations congregate next to the surface of the solid to screen the negative charges from one another.

If only univalent Na counterions were present, water molecules were affected by the two attractive forces; on their front, they formed hydrogen bonds to the negatively charged surface; on their rear, they bound sodium cations (Figure 3). If divalent Ca or Mg cations coexisted with univalent Na cations, they displaced Na ions from the interface (this result can be explained by Manning's polyelectrolyte theory or by more elaborate treatments, such as Poisson-Boltzmann or Monte Carlo calculations, performed in the authors' laboratories). Water molecules became squeezed at the interface between the negatively charged surface and the divalent cation at their backs.

Both attractive interactions increased. The interpretation of the sign reversal for the ^2H residual splittings is as follows: if water molecules reoriented predominantly around the hydrogen bond (O–H axis) when only Na^+ ions were present, the reorientational axis changed to the stronger metal-oxygen bond (Ca^{2+}–O axis), on binding more strongly divalent calcium ions.

In static terms, this phenomenon is represented by the very strong polarization of water molecules simultaneously bound to a negative center by hydrogen bonding and to a cation through one of the lone pairs. Such a polarization was greatly increased by highervalent cations, and was preparatory, in dynamic terms, to the transfer of the proton (or rather deuteron) from the water oxygen to a negatively charged surface oxygen. The latter was expressed as the familiar high
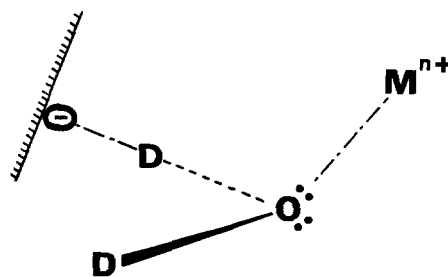

Figure 3.   Geometry for heavy water molecules squeezed between charged aluminosilicate sheet and condensed M^{n+} counterions. The two reorientational axes mentioned in the text are drawn: one is along the hydrogen-bond anchoring the D_2O molecule to the clay surface; the other is along the predominantly electrostatic bond formed between the cation and one of the two oxygen lone pairs.

Brønsted acidity at the surface of clays exchanged with divalent (or higher valent) cations.

ACKNOWLEDGMENTS

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