NOTE

OCTAHEDRAL OR TETRAHEDRAL ISOMORPHOUS SUBSTITUTION: HOW IT AFFECTS WATER AND ACETONITRILE INTERACTION WITH A CLAY, AS SEEN BY NMR

Key Words—^{2}H NMR, Hectorite, Hydration, Montmorillonite, Saponite.

It is possible to ascertain by a simple NMR technique if a clay has tetrahedral or octahedral isomorphous substitution of its structural cations. The basis of the determination is to suspend the clay particles in heavy water and to insert the sample in the probe of a routine high-resolution nuclear magnetic resonance (NMR) spectrometer. In the several tesla-strong magnetic field thus provided, the clay platelets orient themselves within a few minutes (Grandjean and Laszlo 1989; Grandjean and Laszlo 1990). This puts those water molecules that are attached to the clay platelets in an anisotropic environment which in turn endows the quadrupolar ^{2}H and ^{17}O nuclei with non-degenerate transitions. Since the quadrupolar interaction is very large (of the order of magnitude of 0.1–10 MHz), both these nuclei display residual quadrupolar splittings (Grandjean and Laszlo 1989; Grandjean and Laszlo 1990; Delville *et al* 1991), even in the presence of fast exchange between the interfacial water molecules and the bulk solution. The measured splitting D is the product of three terms (Halle and Wennerstrøm 1981). The first includes the quadrupolar coupling constant (e^2 qQ/ h) for the monitored nucleus. The second is the dipolar term (3 cos$^2\Theta_{LD}$ − 1), where Θ_{LD} denotes the angle between the laboratory and the director coordinate systems. The third is the residual anisotropy A, determined by appropriate order parameters, with values between −1 and +1:

$$D = \frac{e^2\ qQ}{4I(2I\ -\ 1)h}(3\ \cos^2\Theta_{LD}\ -\ 1)A \qquad (1)$$

where I is the spin quantum number (I = 1 for ^{2}H). Accordingly, the observed splitting D may have either a positive or a negative sign.

Indeed, the magnitude and the sign of D are both highly sensitive to the content of exchangeable divalent cations (Ca^{2+}, Mg^{2+}) when a typical montmorillonite (Wyoming) is suspended in heavy water. We have interpreted this key initial observation in terms of fast exchange of water molecules between the bulk (no splitting) and two interfacial sites having residual anisotropies A of opposite signs (Grandjean and Laszlo 1989; Delville *et al* 1991). At the clay interface, water mol-

ecules either form hydrogen bonds to the negatively charged surface or interact with exchangeable cations. The presence of divalent cations favors the latter cationic site (Grandjean and Laszlo 1989; Delville *et al* 1991). When clay minerals having isomorphous substitution confined to a single site, either octahedral or tetrahedral, are suspended in water, the resulting residual quadrupolar splittings are nearly-invariant to the relative amounts of univalent and divalent interlamellar counterions: with hectorite, saponite, and another montmorillonite (from Gonzales County, Texas), the water deuteron splitting is only weakly affected by the presence of exchangeable cations (Grandjean and Laszlo 1994a). To explain all our previous data, we have assumed two different water sites at the clay interface, with octahedral and tetrahedral cation replacement, respectively (Grandjean and Laszlo 1994a).

We report here another confirmatory test on the presence of two water interfacial sites with opposite anisotropies (A): two clays having, on the one hand only tetrahedral substitution and on the other, only octahedral substitution, are co-suspended in water. Since the D$_2$O molecules exchange fast between the bulk and the interfacial sites on both types of clay, it is expected in such a situation that they will scan sites with opposite anisotropies A. Thus a weighted average residual quadrupolar splitting is predicted with an absolute value smaller than those characteristic of each clay taken separately.

^{2}H NMR (at natural abundance) splittings were recorded as previously described with a Bruker AM 300 WB spectrometer (B$_0$ = 7.05 T). In typical experiments, 5000 transients were acquired in 16 K points, with a spectral width of 1000 Hz, and were transformed with 32 K points (digital resolution = 60 mHz). Deconvolution procedures assuming all lineshapes to be Lorentzian, were applied if the doublet was insufficiently resolved (Grandjean and Laszlo 1989; Delville *et al* 1991). Hectorite (from Hector, California), purified according to standard procedure (Fripiat *et al* 1982), is affected by isomorphous cationic substitution in the octahedral layer only (Xu and Harsh 1992). A montmorillonite sample (from Gonzales County, Texas) has

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Table 1. Experimental and calculated water deuteron splittings in clay suspensions.

| Clay(s)[1] | Substitution | Experimental values (Hz) | Calculated values (Hz) sign of A | |
			Opposite	Same
GZ[2]	oct.	15.2		
SA[2]	tet.	9.7		
HENa[2]	oct.	17.0		
GZ + SA	oct + tet.	±0	2.8	12.5
HENa + SA	oct + tet.	±0	3.7	13.4

[1] 150 mg/5 ml H_2O; T = 299 K.

[2] GZ: montmorillonite (Gonzales County, Texas); SA: saponite (Ballarat, California); HENa: Na-exchanged hectorite (Hector, California).

Table 2. Experimental and calculated acetonitrile deuteron splittings in clay suspensions.[1]

| Clay(s) | Substitution | Experimental values (Hz) | Calculated values (Hz) sign of A | |
			Opposite	Same
GZ[2]	oct.	12.9		
SA[2]	tet.	33.5		
HENa[2]	oct.	11.5		
GZ + SA	oct + tet.	6.0	10.3	23.2
HENa + SA	oct + tet.	9.7	11.0	22.5

[1] 80 mg/3 ml H_2O–CD_3CN (95/5; V/V); T = 299 K.

[2] GZ: montmorillonite (Gonzales County, Texas); SA: saponite (Ballarat, California); HENa: Na-exchanged hectorite (Hector, California).

the same structural feature (Olis and Douglas 1990). Conversely, saponite (from Ballarat, California) shows cation replacement by another of lower oxidation state, in the tetrahedral layer only (Olis and Douglas 1990). Natural clays were directly used but hectorite which was obtained under its sodium-saturated form.

Thus, aqueous mixtures of saponite and Gonzales County montmorillonite, or of saponite and hectorite, will include both "tetrahedral" and "octahedral" water binding sites. With water molecules exchanging fast between free (i.e., bulk) sites and bound sites of either or both types, only a weighted average residual splitting

$$D = \sum_{i=1}^{3} p_i D_i$$ will obtain, where the p_i's are the mole

fractions and the D_i's the characteristic splittings in each of these states (D_1 is zero for the bulk).

Examination of the data in Table 1 shows that the only tenable assumption is that octahedral and tetrahedral substitutions lead to water attachments with anisotropies A of opposite signs. The absence of observable residual quadrupolar splitting (within a resolution of the bandwidth, i.e., ±5 Hz) rules out the converse hypothesis. Furthermore, the ^2H NMR spectrum of a co-suspension of sodium-exchanged hectorite and montmorillonite (GZ) in water exhibits a quadrupolar splitting of 16.1 Hz, the mean value of the splitting for isolated clays (Table 1). Therefore residual anisotropies have the same sign for these clays with isomorphic substitution in the octahedral layer.

When montmorillonite (Wyoming) clay is suspended in aqueous solution of a deuterated polar organic solvent (CD_3CN for instance), the magnitude and the sign of the cosolvent deuteron splitting is also affected by the content of exchangeable calcium ions (Delville et al 1991). Therefore a similar dependence of the isomorphic substitution on the ^2H quadrupolar splitting is also expected in these systems and experiments as reported in Table 1 have been performed with water-acetonitrile-d_3 suspensions (Table 2).

Again, residual anisotropies of the acetonitrile deuterons display opposite signs when cation isomorphic substitution occurs either in the octahedral or in the tetrahedral layer. As noted above, it is assumed that the clay behavior is purely additive. Thus small differences between the observed and calculated values may be due to this approximation. More results on saponite suspensions in water-acetonitrile mixtures have been published elsewhere (Grandjean and Laszlo 1994b).

Other polar molecules attached at a clay interface may give rise to similar results, we venture to predict.

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