# Dynamics and Ordering of Intercalated Water in Layered Metal Hydroxides

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# Dynamics and Ordering of Intercalated Water in Layered Metal Hydroxides

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The interaction of intercalated water molecules with Mg–Al–NO$_3$ double-metal hydroxides has been studied by using NMR spectroscopy. The water molecules are hydrogen-bonded to the hydroxyl groups in the layers causing them to be oriented perpendicular to the plane of the layers, while retaining their translational mobility. The strength of the bonding between the interlayer water and the layers, as evidenced by the temperature at which a motionally averaged Pake doublet first appears, is related to the interlayer spacing available for intercalation of the guest water molecules.

## Introduction

The interaction of water with oxide lattices has been extensively studied for materials such as silica gel,[1] clays,[2] and zeolites.[3] However, no similar study exists for hydroxide lattices. The reason is, perhaps, that hydroxide lattices are usually close-packed and therefore inaccessible to water molecules. There is, however, one class of compounds which exhibits an "open" hydroxide lattice, the anion-intercalating double-metal layered hydroxides (DMLH).[4]

DMLH compounds are exemplified by the mineral hydrotalcite and consist of brucite-type hydroxide layers, M$^{II}$(OH)$_2$, in which a portion of the divalent cations have been substituted by trivalent cations. Thus, the entire layer bears a positive lattice charge which is balanced by anions which separate the hydroxide layers and make the interlayer accessible to water molecules. Both the nature of the layer cations and the intercalating anion can be varied, and a number of DMLH compounds exist in nature. These materials have a significant capacity for water, which can be as high as 20 wt %.[5]

The water found in DMLH materials is present in a unique environment. The water molecules are intercalated between metal hydroxide layers to which they are most likely hydrogen-bonded. In addition, they exist in close proximity to the intercalated anions. Thus, the possibility exists that the binding strength of the water molecules depends on the exact chemical nature of the DMLH. Thermal analysis studies have shown that the sorption–desorption characteristics can vary significantly with the nature of the constituting cations and anions, the crystal size, and defects in the layers.[6,7]

This work describes a study of the dynamics and ordering of water molecules in a series of Mg–Al–NO$_3$ DMLH of differing compositions and with different morphological characteristics. A complete physicochemical characterization was undertaken in order to have a defined understanding of the structural properties. The behavior of water in these materials was studied by $^1$H NMR of both powdered and ordered samples. Measurements of the dipolar interactions and relaxation times at various temperatures have been used to deduce the structure, arrangement, and mobility of the water molecules within the interlayer. Differences in the molecular dynamics of water have been noted among the different DMLH compounds studied. Based on these studies a model for the arrangement of water within the interlayer is being proposed.

## Experimental Section

*Synthesis.* Double-metal layered hydroxides of magnesium and aluminum, with the molecular formula [Mg$_{1-x}$Al$_x$(OH)$_2$]- [(NO$_3$)$_x$·$n$H$_2$O], were prepared from the nitrate salts. A mixed solution of the appropriate cation salts in the required molar ratio was coprecipitated with 0.2 M NaOH. The pH of the suspension was maintained at 8.5 during the addition, which required ap-

proximately 1 h. After complete addition the precipitate was allowed to age for 16 h and was then washed with deionized water. Materials corresponding to *x* = 0.20, 0.25, and 0.30 were thus prepared. After washing, each DMLH was hydrothermally treated under autogenous pressure for 18 h at temperatures of 110, 200, and 280 °C, respectively. Thus, a total of nine DMLH materials were prepared and these will be designated throughout the paper by the short-hand notation "DMLH-{*x*,*T*}". For example, DMLH-{0.25,200} refers to a material with the formula [Mg$_{0.75}$Al$_{0.25}$(OH)$_2$][(NO$_3$)$_{0.25}$·$n$H$_2$O] which was hydrothermally treated at a temperature of 200 °C. The samples were hydrated by allowing them to equilibrate with the laboratory air for several days prior to the study. Volumetric water sorption measurements indicated that fully hydrated compounds contained between 5 and 8 wt % water in the interlayer.

The purity and crystallinity of the final materials was monitored by X-ray diffraction with a GE XRD-5 diffractometer using Cu K$\alpha$ radiation and a graphite monochromator. Both random powder samples and oriented samples were measured. For the latter, the specimen was prepared by drying an aqueous suspension of the desired material onto a glass slide at 80 °C. Oriented specimens showed only the [001] reflection.

*Nuclear Magnetic Resonance.* Nuclear magnetic resonance (NMR) studies of the water in the interlayer of fully hydrated DMLH compounds were carried out on a Bruker MSL-300 spectrometer using a high-power proton ($^1$H) probe. The $^1$H observe frequency was 300 MHz. The sample tube was made of Pyrex glass with an outer diameter of 5 mm and was configured perpendicular to the magnetic field. Temperature was controlled between −100 and +100 °C with a Bruker VT system.

Both random powders and oriented samples were studied. Specimens of oriented samples were obtained by first depositing an aqueous suspension of the DMLH onto a glass slide, followed by gentle drying at 80 °C. Specimens prepared in such a manner have the majority of their layers parallel to the surface of the glass slide. The slide was then cut to fit inside a sample tube and could be manually turned with respect to the magnetic field.

Wideline spectra were obtained over a spectral window of 500 kHz with a 90° pulse of 2–4 μs, the recycle time between acquisitions was 10 s, and a line-broadening factor of 100 Hz was used in processing all the spectra. Ordinary single-pulse Bloch decay mode was used for collecting these spectra. For the powder samples, 4–16 scans were generally sufficient to give adequate signal-to-noise ratios. Up to 2000 transients per spectrum were collected for the oriented samples. Proton $T_1$ relaxation times were determined as a function of temperature for various powdered DMLH materials by using the inversion recovery pulse sequence 180°–*t*–90°, where *t* is a variable delay.[8]

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(1) Woessner, D. E. *J. Chem. Phys.* **1963**, *39*, 2783.
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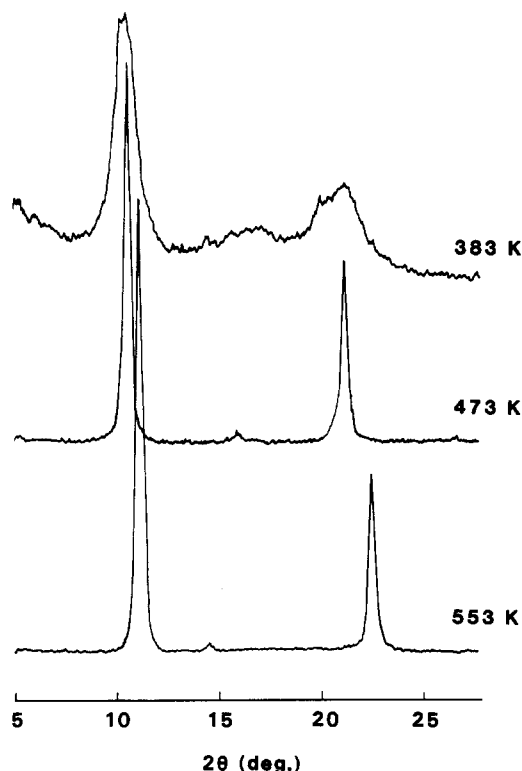
**Figure 1.** XRD patterns of DMLH with $x = 0.25$ after overnight hydrothermal treatment at 110, 200, and 280 °C.
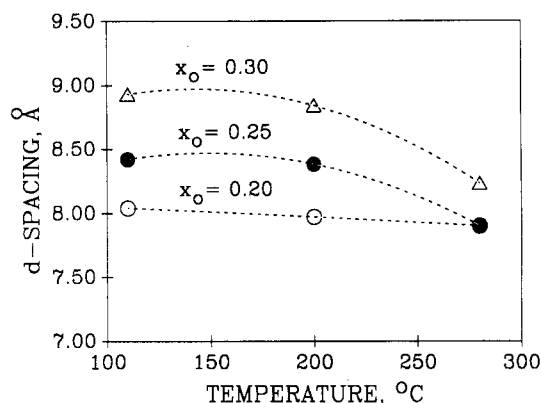


**Figure 2.** Effect of initial layer composition ($x_0$) and temperature of hydrothermal treatment on the layer $d$ spacing of DMLH.

## Results

*Materials.* Syntheses of the DMLH compounds were confirmed by using a combination of XRD, TEM, elemental analyses, and solid-state NMR techniques. These procedures have been described in detail elsewhere.[9] The DMLH compounds were readily formed at room temperature for materials with $0.20 \leq x \leq 0.30$, where $x$ is the atomic ratio of the trivalent cation in the layers. Beyond these limits, the aluminum cation cannot be substituted into the brucite layer without appreciable distortion of the layer thickness or deposition of single oxide impurities.[10]

Although room temperature synthesis was sufficient to form the desired DMLH compounds, these were initially very poorly crystallized. Further treatment under hydrothermal conditions led to recrystallization without loss of structure. Figure 1 shows typical XRD patterns of a DMLH immediately after synthesis and following overnight hydrothermal treatments at 110, 200, and 280 °C. The increasingly sharper patterns observed upon treatment clearly demonstrates a growth in the crystal size with

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**TABLE I: Interlayer Distance and $d$ Spacing of Mg-Al-NO₃ DMLH**

| sample | $x^a$ | hydrothermal treat., °C | crystallite thickness,[b] nm | interlayer dist, Å | $d$ spacing [001], Å |
|--------|-------|-------------------------|------------------------------|--------------------|----------------------|
| 1 | 0.2 | 110 | 9.0 | 3.27 | 8.04 |
| 2 | 0.2 | 200 | 22 | 3.20 | 7.97 |
| 3 | 0.2 | 280 | 22 | 3.13 | 7.90 |
| 4 | 0.25 | 110 | 6.3 | 3.65 | 8.42 |
| 5 | 0.25 | 200 | 17 | 3.61 | 8.38 |
| 6 | 0.25 | 280 | 22 | 3.13 | 7.90 |
| 7 | 0.3 | 110 | 14 | 4.16 | 8.93 |
| 8 | 0.3 | 200 | 16 | 4.07 | 8.84 |
| 9 | 0.3 | 280 | 18 | 3.46 | 8.23 |

$^a x = [Al^{3+}]/[Mg^{2+} + Al^{3+}]$.  $^b$ By XRD line broadening.
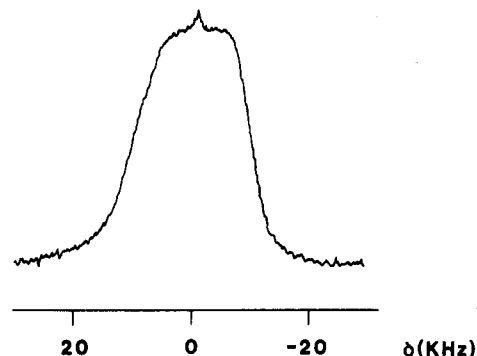


**Figure 3.** $^1$H NMR spectrum of dehydrated DMLH-{0.25,200}. Broad signal corresponds to layer hydroxyl groups.

increasing severity of treatment.

In addition to the higher crystallinity, hydrothermal treatment led to subtle changes in the structure of the DMLH compounds. Figure 2 shows the effect of hydrothermal treatment on the [001] $d$ spacing of materials with $x = 0.20$, 0.25, and 0.30. In general, an increase in treatment temperature resulted in a decrease in the d-spacing. Since layer thickness remains essentially constant within the range of substitution studied, a significant variability in interlayer distance can be achieved by this technique and changes of up to one angstrom are possible with essentially the same layer material. Table I summarizes the synthesis conditions and the resulting characteristics of the DMLH's studied.

*Nuclear Magnetic Resonance.* The $^1$H NMR powder spectrum of dehydrated DMLH-{0.25, 200}, obtained at room temperature, is shown in Figure 3. Similar spectra were observed at other temperatures. Such broad, featureless spectra are characteristic of rigid lattices such as found in the hydroxides in the layers and was found to be typical of all the deydrated materials. In some cases a small, narrow signal (assigned to 0 ppm) was also observed superimposed on the broader line. This narrow signal likely corresponds to freely mobile water on the sample surface or in the probe. Figure 4 shows the powder spectra of the DMLH materials at various temperatures. These spectra represent contributions from all the protons, both framework and interlayer, and no attempt was made at subtracting the framework contribution from the spectra. For all the hydrated materials an additional feature, typical of a Pake doublet powder spectrum,[11] was observed below some temperature, $T_d$. However the temperature $T_d$ varied depending on the sample. In all cases, further lowering the temperature led to a loss of the Pake doublet as the spectrum became a featureless line with no noticeable change in width. At temperatures above $T_d$, the Pake doublet disappeared and an increased sharp central component, which was superimposed on the broader signal, appeared.

Measurements were conducted using an oriented sample of DMLH-{0.25,200} in which the plane of the interlayer was oriented with respect to the magnetic field. This sample was chosen because the Pake doublet was evident at room temperature. A typical set of these results is shown in Figure 5. Due to the small amount

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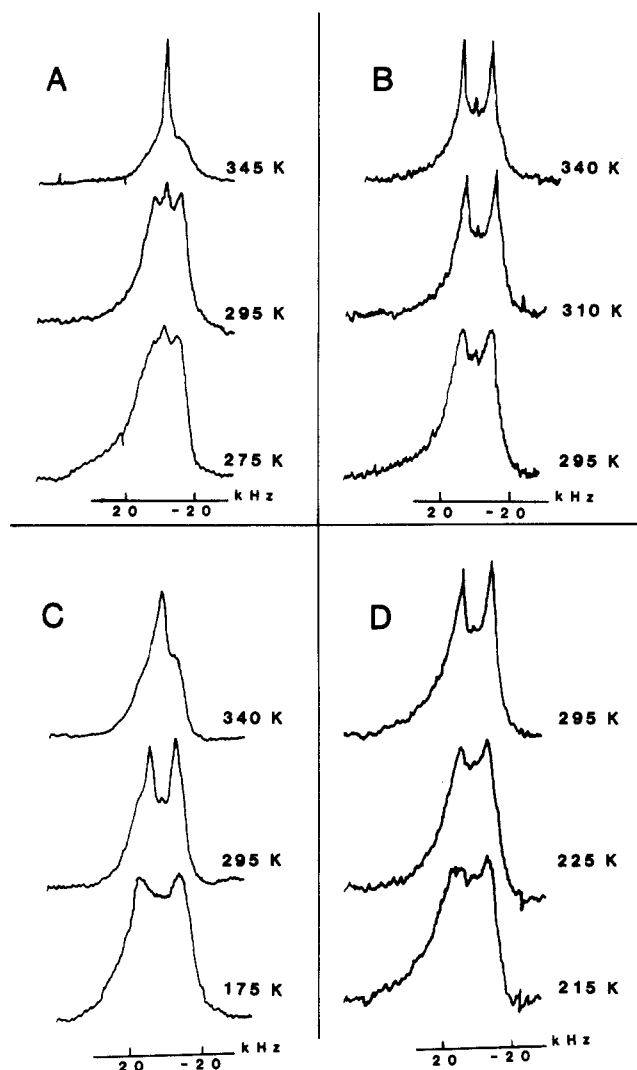
**Figure 4.** Effect of temperature on NMR line shape for various water-loaded DMLH. Spectra correspond to (A) {0.20, 110}; (B) {0.20, 280}; (C) {0.30, 110}; and (D) {0.30, 280}.
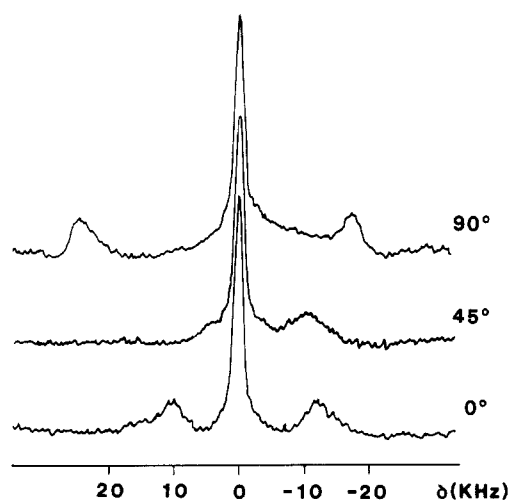


**Figure 5.** Effect of angular layer orientation with respect to magnetic field on $^1$H NMR spectra for DMLH-{0.25,200}. Angle listed in figure refers to angle between magnetic field and layer plane. Central line is due to probe background.

of sample used in such experiments, the spectra are dominated by a large central line which was determined to be due to probe background. The central line is surrounded by two smaller lines corresponding to the Pake doublet which were observed to shift in position depending on the orientation of the DMLH crystals.
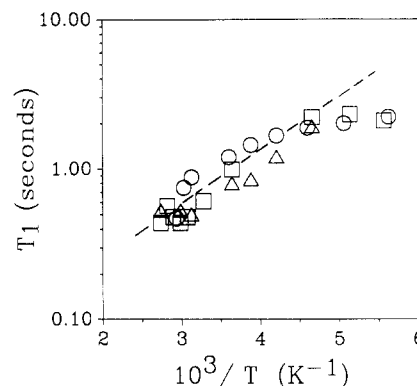


**Figure 6.** Dependence of spin–lattice relaxation time ($T_1$) on temperature for DMLH materials: (O) {0.20, 280}; (□) {0.20, 200}; (△) {0.25, 200}.

Because of the uniform orientation of the crystals, the spectrum observed should be similar to that of a single crystal and can be defined by two lines at positions defined by the equation[11]

$$H = H' + \alpha(3 \cos^2 \theta - 1)$$

where $H'$ is the resonance position due to the Zeeman interaction alone, $\alpha$ is $^3/_2(\mu r^{-3})$, and $\theta$ is the angle between the internuclear H–H vector and the laboratory magnetic field.

The $T_1$ relaxation times for water in various DMLH compounds were determined as a function of temperature by using the inversion recovery pulse sequence $180°-t-90°$, where $t$ is a variable delay. These are shown in Figure 6 as ln ($T_1$) vs $1/T$ plots at 300-MHz frequency. Because of the high resonance frequency of the spectrometer used, the $T_1$ relaxation curve covered only the slow motional region of the spectrum and part of the relaxation minimum. In the slow motional region

$$T_1 = C\tau_c = C\tau_0 \exp(E_a/RT)$$

where $C$ is a constant, $\tau_c$ the correlation time of the motion, and $\tau_0$ the correlation time at infinitely high temperature. Use of this equation allows for the determination of the motional activation energy from the straight portion of the plot. These values are approximately equal for all the DMLH compounds, i.e., approximately 4 kJ/mol.

**Discussion**

As first demonstrated by Pake and Gutowsky,[11,12] pairs of nuclei with spin $^1/_2$ in a rigid matrix give rise to a doublet signal due to intramolecular dipolar coupling. For rigid pairs, such as found in the water of hydration of gypsum, $CaSO_4 \cdot 2H_2O$, the splitting constant corresponds to $3(\mu r^{-3})$, while for pairs with restricted $C_{2v}$ rotational mobility, it corresponds to $3/2(\mu r^{-3})$, where $\mu$ is the magnetic moment of the nuclear spin and $r$ is the nucleus to nucleus distance. In the DMLH materials, the dipolar splitting was observed below $T_d$ and corresponded to about 20–22 kHz. It has been reported that in the rigid lattice a splitting of ca. 46 kHz is expected,[11] indicating that the water molecules in the DMLH are oriented but still retain some degree of activated motional freedom around the $C_{2v}$ axis.

Based on this approach, and assuming a completely rigid lattice, it was possible to calculate the H–H distances for various DMLH. By assuming a H–O bond length of 0.96 Å,[13] the H–O–H angle can be estimated. These are shown in Table II along with the corresponding value for free water. The water molecules intercalated in the DMLH's appear to be slightly distorted, having a longer H–H distance than observed in free water. Such distortions have been suggested for intercalated water in layered transition metal dichalcogenides.[13] It is surprising that the calculated geometry of the intercalated water, and thus the distortion, was similar in all the DMLH. If the distortion were due to the restricted environment in which the water molecules are found

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**TABLE II: Splitting Constants, Calculated H-H Distance, and Calculated H-O-H Angle for Mg-Al-NO₃ DMLH**

| sample | $x^a$ | hydrothermal treat., °C | $\Delta H_0$, kHz | H–H distance, Å | H–O–H angle, deg |
|---|---|---|---|---|---|
| 1 | 0.2 | 110 | 22 | 1.60 | 113 |
| 2 | 0.2 | 200 | 20.9 | 1.63 | 116 |
| 3 | 0.2 | 280 | 22 | 1.60 | 113 |
| 4 | 0.25 | 110 | | | |
| 5 | 0.25 | 200 | 21.4 | 1.61 | 114 |
| 6 | 0.25 | 280 | | | |
| 7 | 0.3 | 110 | 21.1 | 1.62 | 115 |
| 8 | 0.3 | 200 | | | |
| 9 | 0.3 | 280 | 21.7 | 1.60 | 113 |
| free water[b] | | | | 1.51 | 105 |

$^a x = [Al^{3+}]/[Mg^{2+} + Al^{3+}]$. $^b$ From ref 12.
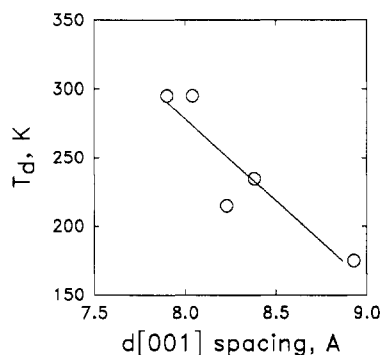


**Figure 7.** Pake doublet temperature, $T_d$, plotted versus $d$[001] spacing for various DMLH materials.



**Figure 8.** Effect of angular layer orientation with respect to magnetic field on line pair separation for DMLH-{0.25,200}. Solid line corresponds to predicted separation according to Pake's treatment.



**Figure 9.** Proposed arrangement of interlayer water in DMLH.

within the layers, different degrees of distortion would be expected depending on the interlayer spacing. An alternative, and perhaps more likely explanation, is that there really is no such distortion, but rather that wobbling motions of the water molecules serve to reduce the observed dipolar splitting.[14] Pake's treatment is principally applied to totally rigid systems. In this case it is known that the water is not totally rigid since it was observed to be desorbed at temperatures around 110–150 °C, indicating that the interlayer water retains significant translational mobility. Thus, some wobbling motion may also be present resulting in the smaller splitting constant rather than the 23 kHz expected for solely $C_{2v}$ rotation.

At low temperatures no fine structure was observed in the proton spectrum resulting in a signal similar to rigid lattice water dominated by both intermolecular and intramolecular dipolar coupling. At higher temperatures, at or above $T_d$, the intermolecular contribution is possibly averaged by rapid translational motion so that the intramolecular interactions between the two spins of a single water molecule dominate the spectra.

Muller-Warmuth[15] has observed similar behavior for intercalated water in hydrated alkali-metal chalcogenides, also a layered material, and related the temperature of appearance of the Pake doublet ($T_d$) to the enthalpy of hydration of the various alkali-metal ions studied. Similarly we can relate $T_d$ to the interlayer distance in the DMLH. Figure 7 shows that a clear relationship exists between the measured $d$[001] spacing, as measured by XRD, and $T_d$. Larger $d$ spacings result in lower $T_d$. This can be intuitively explained as related to the strength of the hydrogen bonding between the water molecules and the hydroxides in the layers. Larger $d$ spacings result in weaker water–hydroxyl H bonding and the averaging of the intermolecular dipolar interactions is observed at a lower temperature.

From the value for $r$ obtained from the powder spectra measurements, the orientation dependence of the signal splitting depicted in Figure 5 can be readily predicted, as shown in Figure
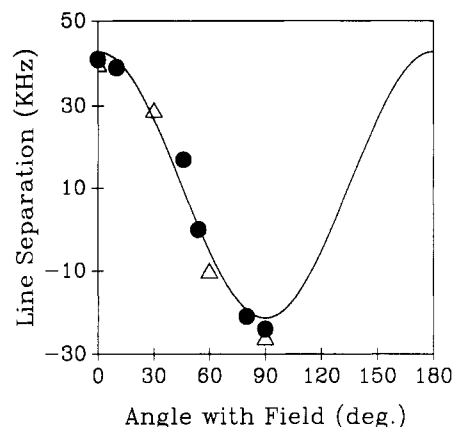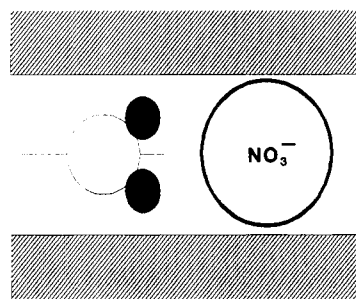
8. Comparison of the predicted and experimental values show excellent agreement for $\theta_{crystal} = \theta_{predicted} + 90°$, suggesting that the interlayer water in DMLH compounds is oriented with its plane of symmetry aligned perpendicular to the [001] plane of the layers, as depicted in Figure 9. The observed spectra thus corresponds well with a model of partially oriented water molecules retaining activated motional freedom around the $C_{2v}$ symmetry axis.

The orientation of the water and the barrier to free rotation is likely due to hydrogen bonding between the hydrogen in the water molecules and the oxygen in the layer hydroxide groups. Miyata[16] has observed evidence for such hydrogen bonding in DMLH's using IR spectroscopic techniques. His work indicated the absence of isolated hydroxyl groups indicating that all OH groups are hydrogen bonding to the interlayer water. Estimates of the interlayer water geometry from their IR work are in reasonable agreement with our NMR results.

The increased central component observed with increasing temperature may have a dual origin. Some of the interlayer water may move to the outside surface of the crystal and become randomly mobile. However, it has been shown that proton exchange between water molecules (or also in this case layer hydroxyl groups) can also result in a central component and has been shown to be the primary mechanism for similar line narrowing in alkali-metal chalcogenides.[17] We have successfully detected such exchange between intercalated $D_2O$ and the layer hydroxyl groups at 90 °C via infrared spectroscopy;[18] however, it is not clear whether this exchange is fast enough to account for the narrow signal at high temperature.

To a first approximation all the DMLH materials showed similar relaxation behavior and similar values of $T_1$, with the room temperature $T_1$ values ranging between 0.6 and 0.8 s. This is similar to what has been reported for liquid water and intercalated water in cationic layers. The value of motional activation energy

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(18) Marcelin, G., unpublished results.

of the water was surprisingly low, 4 kJ/mol, when compared to reported values for structurally similar materials. For example, in cationic monolayer hydrates motional activation energies for intercalated water have values between 13 and 30 kJ/mol.[17,19] This low value is indicative of the rapid translational mobility of the water within the interlayers. This mobility is present in spite of the strong hydrogen bonding which orients the water molecules and most likely occurs via a "jumping" type mechanism between adjacent H-bonding sites.

Although a relaxation minimum cannot be determined from the relaxation time–temperature plot, i.e., Figure 6, it lies above 370 K. Thus, a lower value for a room temperature diffusion coefficient, $D^{RT}$, may be calculated from the correlation times and assuming only two-dimensional translational motion according to[20]

$$D^{RT} = d^2/2\tau$$

where $d$ is the distance between "jumps" from one hydroxide group

to the next (taken to be about 3 Å) and $\tau$ is the correlation time at room temperature. This yields $D^{RT} = 3 \times 10^{-11}$ m²/s, comparable to some of the diffusion coefficients described for monolayer hydrates.[17,21] In view of the observed differences in the temperature behavior of the spectra, differences must exist in the relative diffusivity of interlayer water depending on the layer composition and hydrothermal treatment. However, because of the inaccuracies inherent in our estimation, we cannot measure these differences. The reported value of the diffusion coefficient should not be taken to be more that simply an order-of-magnitude estimate. More precise relaxation minima will be required for an accurate value of $D^{RT}$.

**Registry No.** [Mg$_{0.8}$Al$_{0.2}$(OH)$_2$][(NO$_3$)$_{0.2}$·$n$H$_2$O], 110780-86-4; [Mg$_{0.75}$Al$_{0.25}$(OH)$_2$][(NO$_3$)$_{0.25}$·$n$H$_2$O], 110780-88-6; [Mg$_{0.7}$Al$_{0.3}$-(OH)$_2$][(NO$_3$)$_{0.3}$·$n$H$_2$O], 117150-69-3.

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# Fresh Look at Transport in Perfluorosulfonate Ionomers: Ultramicroelectrode Investigations of Nafion and the Dow Ionomers

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Chronoamperometry at ultramicroelectrodes is a powerful and convenient technique for the determination of apparent diffusion coefficients and concentrations of electroactive cations ion-exchanged into Nafion and Dow perfluorosulfonate films. This technique offers tremendous advantages over the conventional electrochemical methods, which employ film-coated macrosized electrodes. These advantages stem from the elimination of $iR$ distortion at the ultramicroelectrode and from the ability to determine both the concentration and apparent diffusion coefficient of the electroactive cation from a single experiment. Further improvements over the conventional approach were achieved by eliminating coupled diffusion and migration contributions to the measured current response. Under these conditions, charge is transported via ionic diffusion rather than through electron hopping. Furthermore, the apparent diffusion coefficients decrease with increasing concentration of the electroactive cation in the film. This decreasing diffusion coefficient with increasing concentration was attributed to a bottleneck effect caused by the narrow channels that interconnect the ionic clusters in these ionomers.

## Introduction

Perfluorosulfonate ionomers (PFSI's) are unique ion-exchange materials with outstanding chemical and thermal stabilities.[1] Du Pont's Nafion polymers (structure I in Figure 1) are the most widely investigated PFSI's; the Dow Chemical Company has recently described a related series of PFSI's (structure II in Figure 1). Current applications of PFSI's include use in chlor–alkali cells,[2] fuel cells,[3] batteries,[4] and water electrolyzers.[5] All of these applications involve ion or charge transport through a film or membrane of the polymer. Results of numerous investigations of the rates and mechanisms of charge transport in PFSI films and membranes have appeared in the recent literature.[6,7]

One approach for evaluating the transport properties of PFSI's involves electrochemical determinations of apparent diffusion coefficients, $D_{app}$'s, for electroactive cations ion-exchanged into the polymer.[7] Typically, these $D_{app}$'s are obtained by conducting potential step experiments at conventional macrosized electrode surfaces coated with thin films of the polymer. These methods are plagued with problems and pitfalls including the need to

independently determine the concentration of the electroactive cation,[7] distortion of the electrochemical transient by resistance

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