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^2H Solid-State NMR Investigation of Terephthalate Dynamics and Orientation in Mixed-Anion Hydrotalcite-Like Compounds

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The dynamics and orientations of interlayer terephthalate (TA) anions in mixed-anion hydrotalcite-like compounds $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2](\text{A}_y\text{B}_{1-y})_{x/2} \cdot n\text{H}_2\text{O}$, where $\text{A} = p\text{-C}_6\text{D}_4(\text{COO})_2^{2-}$ and $\text{B} = \text{CO}_3^{2-}$] were investigated by ^2H variable-temperature solid-state nuclear magnetic resonance (NMR) spectroscopy. Two dominant 003 d spacings, 7.6 and 14.2 Å, were observed by X-ray diffraction (XRD) in these samples, suggesting that there were at least two interlayer environments. Over the range of layer charges studied ($0.37 \geq x \geq 0.29$), the intensity of the 7.6 Å XRD peak increased with decreasing x , while the intensity of the 14.2 Å peak increased with increasing x . Analysis of ^2H NMR line shapes indicated that the motion of some of the TA anions in every sample could be described as rotational diffusion (RD) about the C–COO[−] axis at temperatures ranging from 245 to 355 K, with the remainder being essentially immobile. The fraction of TA anions exhibiting rotation (X_{RD}), as estimated by ^2H NMR, was positively correlated with the TA content of the interlayer and thus seemed to correspond to the fraction of TA molecules in the 14.2 Å phase. A large difference in X_{RD} was observed between compounds having similar layer charge but different TA mole fractions. At temperatures of ≤ 330 K, X_{RD} increased with temperature. A secondary minimum in X_{RD} , however, was observed for each of the compounds at temperatures between 330 and 350 K. We conclude that the presence of CO_3^{2-} anions in the interlayer regions, rather than layer charge, is the dominant factor affecting the dynamics and orientation of interlayer TA anions.

Introduction

This paper reports an investigation of organic molecules intercalated in the galleries of hydrotalcite-like compounds (HTLCs). Significant attention has been devoted to the synthesis of HTLCs with a variety of metal ions and interlayer anions for possible applications as anion exchangers, catalyst precursors, catalyst supports, and modified electrodes.¹ We have used ^2H nuclear magnetic resonance (NMR) spectroscopy, in combination with XRD and compositional data, to infer the orientation of the intercalated organic molecules with respect to the interlayers and to identify the key factors controlling the observed alignments.

The general formula of an HTLC is $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2](\text{A}^{m-})_{x/m} \cdot n\text{H}_2\text{O}$ where the M^{n+} are metal cations. The structure of these compounds is similar to that of brucite, $\text{Mg}(\text{OH})_2$, with 4.8 Å thick layers of edge-sharing $\text{M}(\text{OH})_6$ octahedra separated by charge-balancing anions and water molecules in the interlayer region.² The HTLCs considered here have the formula $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2](\text{A}_y\text{B}_{1-y})_{x/2} \cdot n\text{H}_2\text{O}$, where the interlayer charge-compensating anions A and B are deuterated terephthalate [TA, $p\text{-C}_6\text{D}_4(\text{COO})_2^{2-}$] and CO_3^{2-} , respectively, and x , which is the mole fraction of Al in the cation suite [i.e., $\text{Al}^{3+}/(\text{Al}^{3+} + \text{Mg}^{2+})$], corresponds to the layer charge of the compound.³ When TA is absent, CO_3^{2-} lies flat in the interlayer region and the spacing between the layers collapses to about 2.4–3.0 Å. In this

configuration, 003 d spacings of 7.2–7.8 Å are observed and the access of other molecules to the interlayer region is minimal. When TA is the dominant charge-compensating anion, interlayer spacings of 3.5–9.4 Å and correspondingly larger 003 d spacings of 8.3–14.2 Å are observed.⁴ The much wider range in interlayer spacings observed with TA is due to the variation in the orientation of the TA anion in response to (1) the charge on the hydroxide layer and (2) the water content of the interlayer region (at least at low layer charge).⁴ Because significantly larger interlayer spacings are associated with TA, the charge-compensating anions and water molecules in the TA phase are more susceptible to exchange by constituents of the bulk solution than those in the CO_3^{2-} phase.

In our initial study of these compounds,⁵ we reported a technique for manipulating the layer charge x and the TA mole fraction in the interlayer anion suite y of synthetic HTLCs by varying the pH of the suspension during the synthesis process. Between pH 10 and pH 7.5, values of x in the solid HTLC product equal to the initial mole ratio in solution were obtained, whereas at more acidic conditions (down to pH 6.8), values of x greater than the solution mole ratio were obtained. Concurrent increases in y were also observed as pH decreased. In our initial study, as well as others,^{4,6} the orientation of the interlayer anions was inferred primarily from powder X-ray diffraction (XRD) measurements of the 003 d spacings. Using XRD, we were able to deduce (1) the presence of two dominant TA orientations in the interlayer region of the HTLCs (i.e., with the C–COO[−] bond directions either parallel or perpendicular to the hydroxide layers) and (2) a correlation of this orientation with x . Given the significantly smaller 003 d spacing for the CO_3^{2-} phase, it

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seemed likely that CO_3^{2-} content also might have affected TA orientation. With the pH-dependent synthesis approach, however, the CO_3^{2-} concentration and layer charge could not be independently varied, nor could their contributions to the orientation of TA in the interlayers be separated.

The roles of CO_3^{2-} content and x in determining TA orientation in HTLCs would be significantly clarified by direct measurements of the relative populations of TA ions in the different interlayer orientations. This information is not necessarily provided by XRD, because only a fraction of TA molecules oriented in the perpendicular direction may be needed to yield a large 003 d spacing. If we suppose that the trajectories of TA molecular motion in the perpendicular orientation are different from the trajectories in the parallel orientation, it follows that the desired information on TA populations could be obtained through solid-state NMR experiments that differentiate between TA molecules on the basis of their molecular dynamics. Anisotropic chemical shift and dipolar interactions revealed in ^{13}C - and ^1H -nuclear magnetic resonance (NMR) line shapes have previously been used to investigate the dynamics and orientation of H_2O and CO_3^{2-} in both powdered and oriented thin-film specimens of Mg/Al hydrotalcites.^{7–9}

In this paper, we demonstrate that ^2H NMR spectra of deuterated TA molecules display a sensitivity to dynamics that can be used to differentiate and quantify TA molecules in different interlayer environments. Specifically, the molecules in a parallel orientation have different rates and trajectories of motion than TA molecules in a perpendicular orientation. Following a well-established strategy,^{10,11} analysis of a series of ^2H line shapes collected across a range of temperatures provides detailed information about interlayer TA orientation and dynamics that is either unobtainable or only indirectly available from XRD measurements of the 003 d spacings. In particular, our results suggest that the presence of interlayer CO_3^{2-} , rather than layer charge, is the dominant factor controlling the orientation of TA in these HTLCs.

Experimental Section

a. Sample Synthesis. Samples were prepared under ambient pressure and atmosphere following the method of Kukkadapu et al.⁵ with minor modifications. Initially, 4.75 g (0.027 mol) of deuterated terephthalic acid [$p\text{-C}_6\text{D}_4(\text{COOH})_2$, ring- d_4 98%; Cambridge Isotope Laboratories, Inc.] was added to a beaker containing 55 mL of deionized water. While this suspension was stirred, 13 mL (0.17 mol) of freshly prepared 50% NaOH was added dropwise over a 30 min period to convert the acid to TA and allow it to dissolve. To this, 63 mL of a solution containing 17.6 g (0.07 mol) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) and 10.5 g (0.028 mol) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich), corresponding to a Mg/Al mole ratio of 2.5:1, was added dropwise while stirring the suspension vigorously. When the suspension pH reached 10, an aliquot was removed and addition of the Al and Mg solution was continued. At pH 7.5 and ~ 6.8 , additional aliquots were removed. The three suspensions were then aged overnight at about 347 K. After aging, the suspensions were washed with water until free of NO_3^- and dried at 373 K overnight. All samples were analyzed for (1) Mg and Al by inductively coupled plasma atomic emission spectroscopy after digestion in 5% HNO_3 and (2) total- and inorganic-C contents by a conventional C analyzer.¹² Finally, the samples were checked for phase purity by powder XRD (smear mounts on zero-background slides, $\text{CoK}\alpha$ X-rays).

b. ^2H NMR Spectroscopy. Solid-state ^2H NMR spectra were acquired on a Varian Unityplus-500 spectrometer at 76.7 MHz

(11.74 T) using a variable-temperature (VT) home-built probe. The rotors containing the samples were capped tightly to minimize irreversible removal of interlayer water that could affect the orientation of the interlayer TA ions. Temperatures could be controlled to within ± 0.5 K over the range 80–355 K. One-dimensional spectra were acquired with a solid-echo sequence¹³ using 90° pulse lengths of 3.0–4.0 μs , 30 μs τ interpulse distances, and delays between acquisitions of 5–60 s. The ^2H two-dimensional (2-D) exchange experiments were acquired with a four-pulse sequence¹⁴ having 90° pulse lengths of 3 μs , 54.7° pulse lengths of 1.8 μs , a 20 μs pulse-echo delay, and a mixing time of 2 ms. The 2-D data set consisted of 256 points in the t_2 dimension and 64 free-induction decays (FIDs) in the t_1 dimension. Each signal in the t_1 dimension is the average of 1024 scans with a delay of 4 s between scans. Pure absorption-mode spectra were obtained according to the method of States et al.¹⁵ After the 2-D Fourier transform, slices in t_2 were individually phased.

The motions of the TA molecule we consider here have been modeled as stochastic hops between a finite number of allowed orientations. In computing theoretical ^2H NMR line shapes for comparison with experimental spectra, we have assumed that the quadrupolar coupling tensor of the deuterons on the TA phenyl ring are axially symmetric, with the z direction of the quadrupolar principal axis system (PAS) collinear with the C–D bond axis. We further assume that the reorientation of the molecule does not modulate the three principal values of the quadrupolar coupling tensor. In terms of NMR parameters, therefore, the effect of the motion of the molecule is the stochastic, anisotropic reorientation of the quadrupolar PAS with respect to a laboratory-fixed coordinate system. The NMR line shape of a deuteron hopping stochastically between a finite number of discrete orientations can be computed exactly.¹⁶ In the computations reported here, we have used a modification of the standard treatment for the case where the ^2H signal is detected with a two-pulse echo.^{17,18}

Results

a. 003 d Spacing and Chemical Composition. Figure 1 shows the powder-XRD patterns of HTLC-1, HTLC-2, and HTLC-3; XRD 003 d spacings are given in Table 1. The HTLC-1 sample, which was synthesized at pH 10, showed peaks corresponding to a 7.6 Å phase. The XRD pattern for HTLC-2, which was synthesized at pH 7.5, was similar to that of HTLC-1, except for the emergence of a minor peak at 14.2 Å and an apparent decrease in the d spacing of the “7.6 Å phase” caused by an overlapping second-order reflection of the 14.2 Å peak. The XRD pattern of the HTLC-3 sample (synthesized at pH 6.8), on the other hand, was dominated by peaks due to the 14.2 Å phase, and no peaks related to the 7.6 Å phase were observed. Our earlier XRD data for similar samples (i.e., Mg/Al 2:1) showed the coexistence of 7.3 and 14.2 Å d spacings in samples synthesized at pH = 7.5.⁵ The 14.2 Å d spacing is attributed to a phase having interlayer TA anions oriented with the C–COO $^-$ bond axis *perpendicular* to the hydroxide layers.⁶ The 003 d spacing of 7.6 Å is close to those observed in hydrotalcites with interlayer CO_3^{2-} anions.¹ Other work has suggested that interlayer TA anions in air- or oven-dried low-charge HTLCs with 8.2 Å 003 d spacings are oriented with the C–COO $^-$ bond axis *parallel* to the hydroxide layers.⁴

The chemical compositions of the prepared samples are given in Table 1. Significant quantities of CO_3^{2-} were present in the samples synthesized at pH 10 and 7.5. Since no CO_3^{2-} was added intentionally during the synthesis, the detected amounts

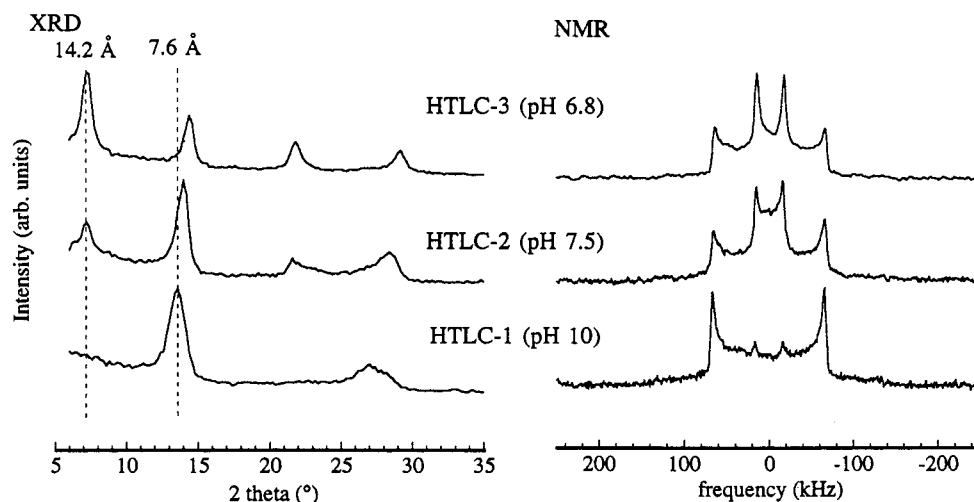


Figure 1. Powder-XRD patterns (left) and ^2H NMR spectra (right) of HTLCs, acquired at room temperature.

TABLE 1: HTLC Structural and Compositional Data

sample	<i>d</i> spacing, ^a Å	composition, wt %				<i>x</i> ^c	<i>y</i> ^d	anion charge distribution, ^e mol %			
		Mg	Al	TA ^b	C _{inorg}			TA	CO ₃ ²⁻	HCO ₃ ⁻	charge balance ^f
HTLC-1 (pH 10.0)	7.6	18.1(0.1)	8.2(0.4)	15.4(0.4)	1.03	0.29(0.01)	0.51(0.01)	60	23	17	1.00
HTLC-2 (pH 7.5)	7.6, 14.2	16.7(0.1)	8.0(0.3)	17.64(0.01)	0.78(0.01)	0.30(0.01)	0.62(0.01)	71	15	14	1.00
HTLC-3 (pH 6.8)	14.2	13.7(0.1)	9.0(0.4)	24.46(0.01)	0.19(0.01)	0.37(0.01)	0.90(0.01)	87	9	-	0.97

^a Based on d_{003} peak (i.e., assuming a three-layer polytype). ^b Based on difference of total- and inorganic-C contents. ^c x of starting solution is 0.286. ^d Moles TA divided by the sum of the moles of TA and C_{inorg}. ^e CO₃²⁻ and HCO₃⁻ fractions assigned to fit x values. ^f Sum of equivalents of TA, CO₃²⁻, and HCO₃⁻ divided by charge from Al³⁺ substitution (all calculated on a unit cell basis).

were either introduced by the NaOH solution or absorbed from the atmosphere during and after preparation of the starting TA solution. The two samples also had similar layer charges of $x = 0.3$. However, the fraction of the layer charge compensated by CO₃²⁻ and HCO₃⁻ decreased from 34% to 24% in going from pH 10 to pH 7.5, as expected from corresponding pH-related decreases in the amounts of solution-phase CO₃²⁻ available for incorporation into the interlayer region.¹⁹ In accordance with the XRD results, the composition of HTLC-3 (synthesized at pH 6.8) differed from the other samples by having a higher layer charge ($x = 0.37$), of which only 9% was compensated by CO₃²⁻. This increase in x can be attributed to changes in relative solubilities of the end-member hydroxides [i.e., Mg(OH)₂ and Al(OH)₃].²⁰ These compositional trends are consistent with our previous results.⁵

We note that the layer-charge and compositional data indicate that the nitrate content of the three HTLCs was negligible. Infrared spectra of other samples we have prepared by this method (unpublished data) support this conclusion. Our samples were prepared at an aqueous nitrate/TA ratio of 1, while samples studied by others⁴ were prepared with aqueous nitrate/TA ratios of close to 10.

b. Room-Temperature ^2H NMR. Movements of a C- ^2H bond characterized by rotational diffusion (RD) rates $k_{\text{RD}} \leq 10^3 \text{ s}^{-1}$ are revealed in ^2H NMR spectra of disordered samples by a line shape consisting of a single Pake pattern.^{11,18,21} The deviations from this pattern in the experimental spectra shown in Figure 1 indicate that some of the TA anions are rotating in all of the samples at room temperature. Of the three specimens, HTLC-1 has the line shape most closely resembling that of a static phenyl deuteron, with a 136 kHz splitting between singularities. This is consistent with the inference from the XRD data that TA molecules in HTLC-1, with only a 2.8 Å spacing between layers, lay nearly flat and have little room for

reorientation. On the other hand, the room-temperature ^2H line shape for HTLC-3 exhibits two prominent resonances at ± 18 kHz (consistent with TA anions undergoing some form of motional process) and a somewhat weaker resonance with a 136 kHz splitting suggestive of static deuterons. The sharp resonances at ± 18 kHz indicate that TA molecules occupy environments that permit rotational motions, which would be the case if TA anions were oriented perpendicular to the layer in the 14.2 Å phase. This result does not preclude the possibility that some TA anions in the 14.2 Å phase are in a parallel, immobile orientation. In sample HTLC-2, which contains both 7.6 Å and 14.2 Å phases, a smaller fraction of the TA anions is oriented perpendicular to the layer than in HTLC-3 and the portion of TA anions that are relatively free to reorient is between that of HTLC-1 and HTLC-3.

c. Variable-Temperature ^2H NMR. Deuterium NMR spectra of the three HTLCs measured for several different temperatures are shown in Figure 2. At the lowest temperatures shown, the ^2H spectra displayed the characteristic Pake pattern of static phenyl deuterons. The amplitude of the ^2H echo decayed to zero at refocusing times of $\geq 300 \mu\text{s}$, but the line shape otherwise showed no dependence on the refocusing time. The spectra of HTLC-3 and HTLC-2 were modified by (1) the appearance of two sharp horns at ± 18 kHz, which increased in relative intensity with the temperature, and (2) the disappearance of the Pake pattern at higher temperatures. The VT ^2H spectra of HTLC-1 are transformed similarly as temperature is increased, with emergence of the resonances at ± 18 kHz at 300 K. However, the static-deuteron spectrum persists at higher temperatures than HTLC-2 and HTLC-3, and the convergence of the spectra to a motionally averaged limit also occurs at higher temperatures.

The VT series of spectra for all samples was completely reproducible after several heating/cooling cycles, indicating that

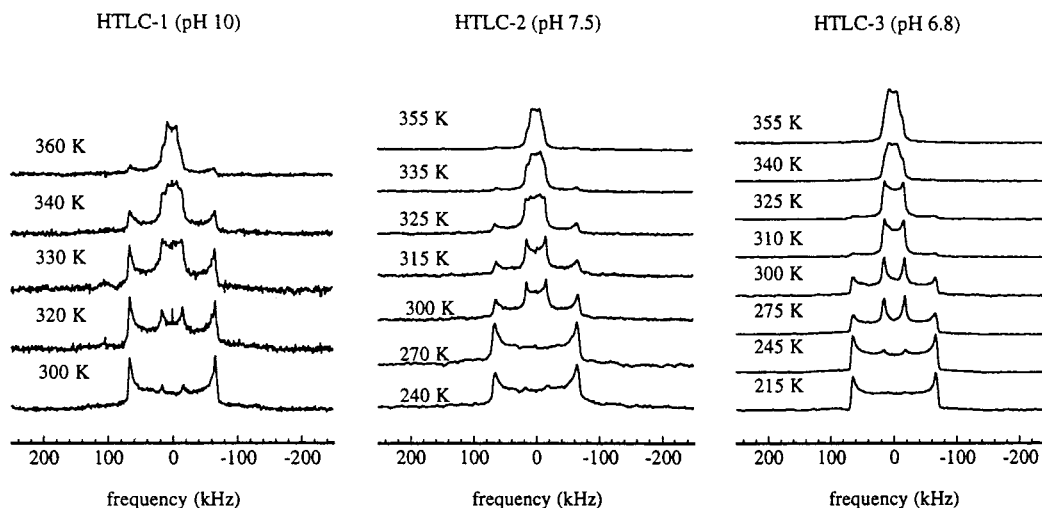


Figure 2. Variable-temperature ^2H NMR spectra measured at 11.74 T of HTLC-1 (left), HTLC-2 (middle), and HTLC-3 (right).

no significant change in the moisture content occurred, but we cannot exclude the possibility of reversible vaporization and condensation of moisture occurring within the sealed sample tube. No differences were found between room-temperature XRD patterns of the specimens collected before and after the VT NMR experiments.

Discussion

a. Structure and Composition. The XRD and chemical data (Figure 1 and Table 1) illustrate the major differences in structure and composition of the HTLCs synthesized from pH 10 (HTLC-1) to pH 6.8 (HTLC-3), with the greatest changes occurring from pH 7.5 (HTLC-2) to pH 6.8 (HTLC-3). These changes include a shift in the dominant 003 d spacing from 7.6 to 14.2 Å, a 28% increase in the layer charge (i.e., from $x = 0.29$ to $x = 0.37$), and a shift in the interlayer anion population from one that contains 40 mol % CO_3^{2-} and HCO_3^- to one that is dominated by TA anions.

As noted by Kooli and Jones,⁴ the perpendicular orientation of TA in HTLCs synthesized from nitrate anion solution matrices is associated with larger values of x . However, in our samples, x changes little from pH 10 to pH 7.5, whereas the TA/ CO_3^{2-} ratio nearly doubles and is accompanied by the emergence of the 14.2 Å peak. It seems, therefore, that interlayer CO_3^{2-} is the main factor controlling the orientation of interlayer TA at pH = 7.5 in our samples. Below pH 7.5, both the increase in x and the further decrease in the amounts of aqueous CO_3^{2-} contribute to the formation of the 14.2 Å phase.

b. NMR Experiments and Simulations. The two end-member HTLCs are each dominated by a single type of interlayer environment for TA at room temperature (i.e., 003 d spacings of 7.6 and 14.2 Å, respectively) and represent the simplest cases to analyze. The XRD and chemical data suggest that TA anions in the interlayers can be binned into at least two groups, one group occupying the 7.6 Å phase and the other occupying the 14.2 Å phase, with different trajectories of motion accessible to each.

Four models that can be imagined for TA motions in the interlayers of the 7.6 and 14.2 Å phases are depicted in Figure 3. The trajectories of these motions result in reorientations (as opposed to translations) of the TA anion. Models A and B of this figure are putative motions of the TA anion in the 14.2 Å phase, with the C—COO[−] bond axis aligned perpendicular to the hydroxide layers. The 180° flip about the C—COO[−] bond directions (model A) portrayed in Figure 3A is a motion

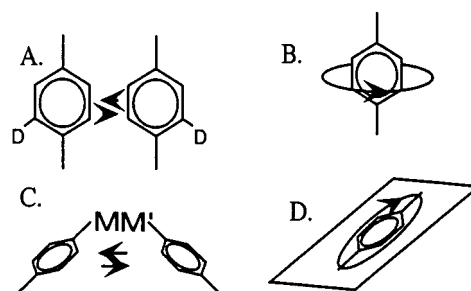


Figure 3. Models of motion assumed in ^2H NMR simulations (see text).

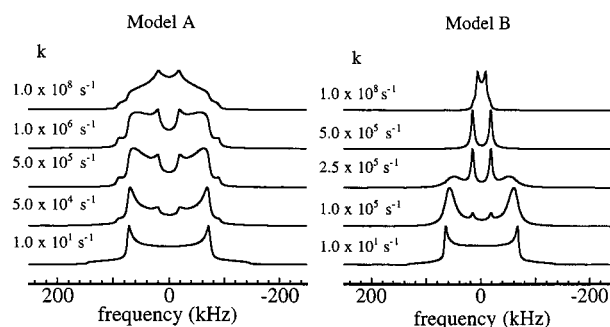


Figure 4. Simulation of ^2H NMR spectra assuming 180° flips about the C_2 axis with two-site exchange rates (left) and stochastic rotational diffusion about the C_2 axis with eight-site exchange rates (right).

previously seen in polymers.²² Figure 3B illustrates a uniaxial RD model (model B), in which the TA anion rotates freely and stochastically about its C—COO[−] bond axis, instead of in discrete 180° jumps. Parts C and D of Figure 3 represent possible TA motions within the restricted environment of the 7.6 Å phase. Model C exemplifies a 60° pivot of the TA anion as it switches coordination with Al^{3+} ions in the hydroxide layer. The motion of TA in model D is stochastic rotation about an axis perpendicular to the plane of the phenyl ring and passing through its center. The C— ^2H bond in models B and D is confined to a cone. Rotational diffusion was approximated in these simulations by nearest-neighbor exchange between eight orientations around the cone, spaced by 45° intervals.

The simulated spectra associated with models A and B are shown in Figure 4. At intermediate rates, i.e., $k_{\text{RD}} \approx 10^5 \text{ s}^{-1}$, both models reproduced the appearance of features at $\pm 18 \text{ kHz}$. At higher rates, model A (180° flips) began to diverge from the higher temperature experimental spectra. Spectra computed

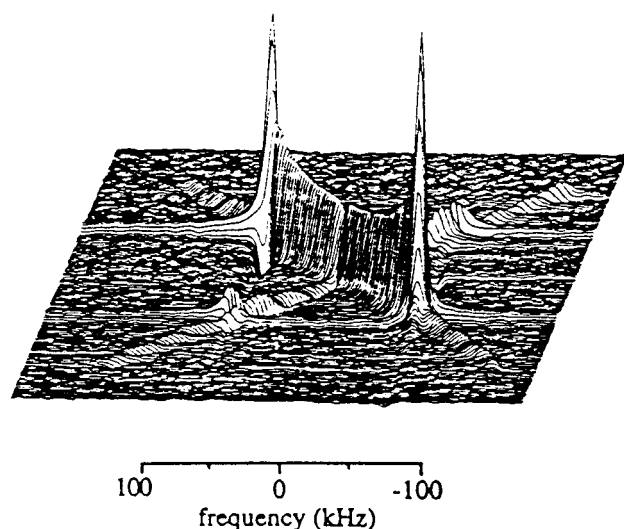


Figure 5. Two-dimensional ^2H -exchange NMR spectrum of HTLC-3 at 250 K

with model B reproduced the experimental data more closely but still diverged in significant ways. In particular, the superposed Pake-like pattern present in the HTLC-1 experimental data at high temperatures was missing from the simulated model B spectra. Spectra computed on the basis of models C and D differed substantially from the experimental spectra and are not included here.

The results of a 2-D ^2H -exchange experiment (Figure 5) provide further proof that the 180° flip motion is not occurring in HTLC-3 even at low temperatures. If such a motion were occurring, the 2-D spectrum associated with model A would contain elliptical ridges¹⁴ and would be readily differentiated from the spectrum for model B. These features were absent from the experimental spectrum. The signal-to-noise ratio, which was achieved with 1 week of instrument time, could not feasibly be improved with further averaging but was sufficient to enable observation of the ellipses had they been present. In addition, the weak signal and the broadening of the diagonal were characteristic of RD, not 180° flips.

Comparison of experimental (Figure 2) and simulated (Figure 4) results reveals that the model B simulations closely match the HTLC-1 experimental data, while those of models C and D do not. On the basis of the room-temperature XRD data indicating a single 7.6 \AA phase in HTLC-1, there would appear to be little room between hydroxide layers in HTLC-1 for TA molecules to rotate freely about the $\text{C}-\text{COO}^-$ bond axis. The room-temperature NMR spectrum of HTLC-1 is dominated by the Pake line shape of a static phenyl deuteron, indicating that most TA molecules are nearly static, with a small but observable RD fraction. As temperatures increase, however, the line shape of TA molecules characterized by RD about the $\text{C}-\text{COO}^-$ bond axis becomes a more prominent component of the overall line shape, suggesting the possible expansion of the interlayer spacing. Other work has shown a correlation between interlayer TA orientation, as inferred from 003 d spacings and ^2H NMR data, and water content, which changed with the length of aging of the HTLC after initial precipitation²³ or with heating of the sample in an open oven.⁴ An increase in the activity of interlayer water with temperature might also expand the 003 d spacings and thereby the fraction of TA anions that are free to rotate. For comparison with the unhindered RD model, we have also computed theoretical spectra for restricted rocking rotations about the $\text{C}-\text{COO}^-$ bond axis of the TA anion. None fit the experimental series as well as the unhindered RD model.

On the basis of the XRD and chemical data and the simulations shown in Figure 4, it is logical to consider fitting the experimental ^2H NMR spectra as a superposition of ^2H spectra from two sets of deuterons, one consisting of deuterons that are static and the other consisting of deuterons moving at different rates in the trajectory implied by model B. We refer to this two-phase description as model E. The expression we use to compute the FIDs for distributions of hopping rates and multiple trajectories is given by

$$S(t) = \sum X_i \int_0^\infty S_i(t, k_i) P_i(k_i) R_i(k_i) dk_i \quad (1)$$

where X_i is the fraction of all deuterons that hop in the i th trajectory, $S_i(t, k_i)$ is the time-domain NMR signal for the deuteron in the i th population group, $P_i(k_i)$ is the normalized probability that a deuteron in the i th population group has the rotational frequency k_i , and $R_i(k_i)$ is the echo-attenuation factor^{11,18} for the i th population of deuterons with rotational frequency k_i .

For model E, eq 1 simplifies to a linear combination of two spectra:

$$\begin{aligned} S(t) &= X_1(T) S_1(t, 0) R_1(0) + X_2(T) S_2(t, k_i) R_2(k_i) \\ &= W_1(T, 0) S_1(t, 0) + W_2(T, k_i) S_2(t, k_i) \end{aligned} \quad (2)$$

where W are weighting factors for the two spectra. To allow for the possibility that TA molecules may convert from being a member of one population to being a member of the second population as the temperature is changed, we have written the occupancy fractions X_1 and X_2 as explicitly temperature-dependent quantities.

According to the customary definition of the attenuation factor, $R_1(0) = 1$. We define the *normalized* spectrum weighting factors $w_1(T, 0)$ and $w_2(T, k_i)$ by the relations

$$w_1(T, 0) = W_1(T, 0) / [W_1(T, 0) + W_2(T, k_i)] \quad (3a)$$

$$w_2(T, k_i) = W_2(T, k_i) / [W_1(T, 0) + W_2(T, k_i)] \quad (3b)$$

Spectral simulations based on model E are shown in Figure 6 for the three HTLCs. The parameters k_{RD} and $w_2(T, k_{\text{RD}})$ associated with the best visual fits to the experimental spectra are listed in Table 2. The estimated occupancy fractions for the rotating population (X_{RD}) are plotted in Figure 7. The uncertainty associated with the estimates of X_{RD} varies significantly with the RD rates (k_{RD}) because of the dependence of X_{RD} on the reduction factor [$R(T, k_{\text{RD}}) = w_2(T, k_{\text{RD}}) / X_{\text{RD}}$]. The relationship between R and k_{RD} is shown in Figure 8 (top), with the shaded region corresponding to the range of k_{RD} values extracted from our fits. A numerical first-derivative plot of $R(T, k_{\text{RD}})$ (Figure 8, bottom) shows that uncertainties in k_{RD} result in the largest uncertainties in R when $\log k_{\text{RD}}$ is between 6 and 7. This region in k_{RD} space corresponds to temperature ranges of 270–330 K.

These results suggest that, at room temperature, $\sim 20\%$ of the TA anions in HTLC-1 are executing rotational motions. This fraction increases to $\sim 80\%$ at 320–330 K before decreasing to $\sim 50\%$ at the highest temperature. One possible explanation for the presence of rotating TA anions in HTLC-1 is that they are sorbed to the external surfaces of the HTLC rather than intercalated between internal surfaces. If only one end of the externally sorbed TA anion were attached, a nonparallel molecular orientation with respect to the hydroxide layers and rotation about the $\text{C}-\text{COO}^-$ bond axis could be envisioned. Assuming the TA concentration per unit of layer surface area is the same on the external surfaces as in the interlayers, the

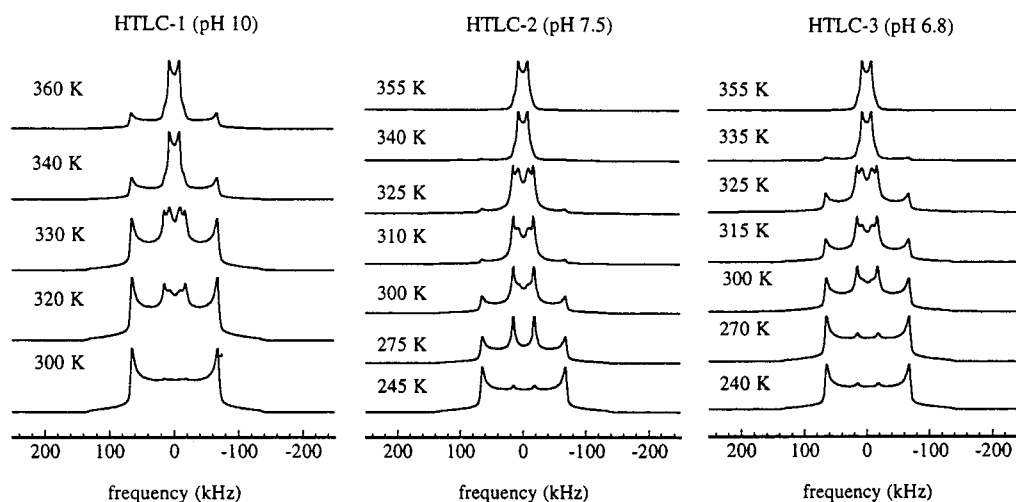


Figure 6. Two-population simulated VT ^2H NMR spectral series (model E) for HTLC-1 (left), HTLC-2 (middle), and HTLC-3 (right).

TABLE 2: Parameters for Two-Population Simulations Using Model E

sample	T (K)	$w_{\text{RD}}(k_{\text{RD}})$	$k_{\text{RD}}(\text{s}^{-1})$
HTLC-1	300	0.01	2.0×10^6
	320	0.15	2.5×10^6
	330	0.25	3.5×10^6
	340	0.40	1.0×10^8
HTLC-2	360	0.50	1.0×10^9
	240	0.02	7.5×10^5
	270	0.03	1.0×10^6
	300	0.25	2.0×10^6
	315	0.40	2.5×10^6
	325	0.50	3.0×10^6
	335	0.80	1.0×10^8
HTLC-3	355	1.00	1.0×10^9
	215	0.00	NA ^a
	245	0.02	7.5×10^5
	275	0.25	1.0×10^6
	300	0.47	2.0×10^6
	310	0.85	2.5×10^6
	325	0.87	3.0×10^6
	340	0.92	1.0×10^8
	355	1.00	1.0×10^9

^a Not applicable.

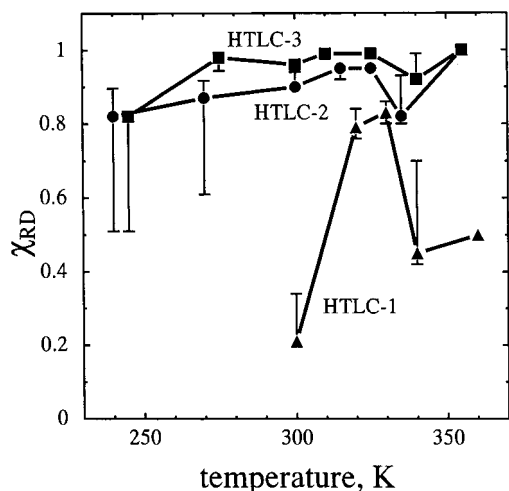


Figure 7. Estimated values of X_{RD} as a function of temperature for the three HTLCs.

fraction of TA molecules on the external surfaces of the particles can be estimated (from XRD peak-broadening measurements of crystallite c dimensions) to be no more than 10–15%. Thus, most of the rotating TA molecules in HTLC-1 can be ascribed

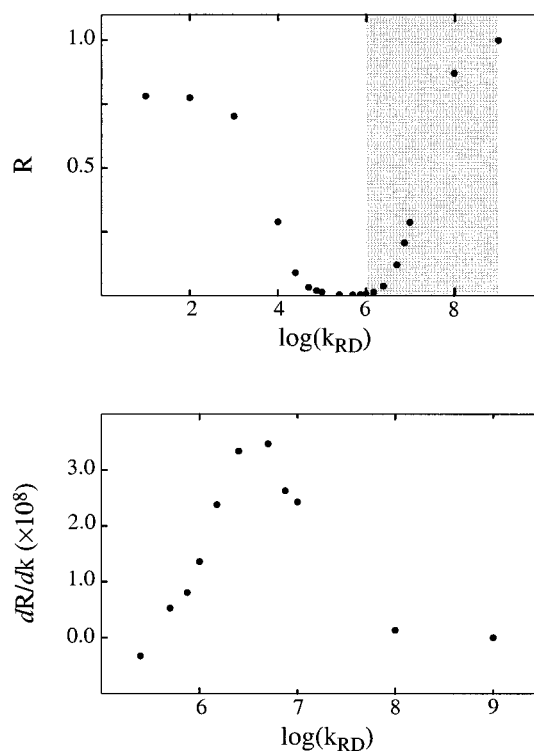


Figure 8. Top: plot of $\log(k_{\text{RD}})$ vs R . Bottom: plot of $\log(k_{\text{RD}})$ vs $\Delta R/\Delta k (\times 10^8)$.

to surface-adsorbed species at room temperature, but not at higher temperatures where the RD fraction increases. This assignment will affect the anion charge distribution given in Table 1.²⁴

For HTLC-2, the NMR results lead to the conclusion that the vast majority of the TA is oriented perpendicularly to the hydroxide layers and can rotate about the C–COO[−] bond axis. Given that the main difference between HTLC-2 and HTLC-1 is a substantial increase in y (i.e., a decrease in the CO₃^{2−} content), it seems that the presence of CO₃^{2−} anions in the interlayer is the main factor restricting TA rotation. Layer charge does not play a role. We note that despite the dominance of the Pake pattern in the 245 K line shape, which is associated with the static deuteron population, the X_{RD} value is still ~ 0.8 because of the small reduction factor corresponding to k_{RD} . A similar line shape for HTLC-1 at 300 K, however, yields an X_{RD} value of ~ 0.2 because the reduction factor is significantly greater.

The NMR and XRD results for HTLC-3 show that nearly all the TA is oriented perpendicular to the hydroxide layer. The only restricted rotational environments in HTLC-3 are the rare sites where adjacent CO_3^{2-} anions might interfere with rotation. Slight decreases in X_{RD} for HTLC-3 and HTLC-2 at temperatures between 330 and 350 K mimic the large decrease seen for HTLC-1.

Given that the activity of H_2O increases with temperature, one might expect that the TA occupancy fractions would change monotonically with temperature. For example, in other work at room temperature involving a homologous series of HTLC samples having similar layer charges ($x = 0.36$) and interlayer anion suite ($\text{TA}/\text{CO}_3 \approx 65:35$),²³ we have seen strong positive correlations between H_2O content (which changes with length of aging during the synthesis procedure), 003 d spacings, and the expression of the ± 18 kHz feature in ^2H NMR spectra. Assuming that increases in H_2O activity and H_2O content have similar impacts on HTLC structure and the orientation of TA, it may be supposed that some of the layers in HTLC-1 would expand to 14 Å upon heating. The ^2H NMR data in Figure 7 suggest that the dynamic population of TA ions in HTLC-1 does rise initially with temperature, as expected, but then falls as the temperature is increased further. This observation could be explained by a scenario in which water is removed from the interlayer and the interlayer spacing collapses to 7.6 Å, in half of the layers forming an ordered mixed-layered phase as the temperature is increased. The sample cell for these NMR studies is tightly sealed, creating the possibility of increased pressures at higher temperatures, which also may influence the spacing between hydroxide layers. A series of XRD patterns obtained at comparable temperatures and pressures would provide a test of this hypothesis. For the HTLC-2 and HTLC-3 samples, which have significantly greater TA concentrations, the 14.2 Å species is the dominant phase over the entire temperature range and little evidence of a collapse of interlayers (i.e., a decrease in the rotating fraction) is observed in the NMR data. The slight decrease in X_{RD} at intermediate temperatures for these two samples is within the uncertainty expected for this estimate given the k_{RD} values.

In binning TA molecules into two groups, each characterized by a single discrete RD rate, we have implicitly assumed that the activation energies associated with the motions can have only two discrete values, depending on the environment occupied by the molecule. By analogy with analyses of ^2H NMR line shapes of complex polymers,²⁵ we note that the molecular dynamics would perhaps be more accurately described by representing the activation energies and rates as distribution functions. The most plausible model for the HTLC case is a bimodal distribution. Based on the correspondence of model E simulations with the experimental data, we infer that the underlying activation energy distributions must be narrow and conclude that the discrete two-site model, while idealized, nevertheless usefully and accurately portrays the dynamic behavior of TA molecules in the HTLC interlayers.

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