

THE ORDERING OF HDTMA IN THE INTERLAYERS OF VERMICULITE AND THE INFLUENCE OF SOLVENTS

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Abstract—X-ray basal reflections of several HDTMA-vermiculites show that when these contain co-adsorbed molecules of HDTMA-Br, their interlayer spacings are ~29.5 Å. After HDTMA-Br has been leached out with ethanol, spacings decrease to ~26 Å, but when exposed to toluene vapor the spacings increase to ~36 Å, and to ~45 Å in toluene liquid. Transmission X-ray diffraction photographs of HDTMA-vermiculites, both with and without co-adsorbed HDTMA-Br, indicate they have highly ordered interlayer structures. The structure of HDTMA-Br-free vermiculite flakes is more open with the interlayer cations arranged in a $3a \times b$ superstructure. In the HDTMA-Br containing HDTMA vermiculite flakes, HDTMA-Br molecules occupy interstitial positions between the HDTMA cations. Swelling in toluene vapor does not disorder the 2-dimensional arrangement of interlayer cations, but disorder does occur in toluene liquid. In toluene vapor, the aliphatic chains of the cations remain partially interdigitated, but in toluene liquid the interdigitation disappears. In response to the layer-charge density, the organization of the interlayer HDTMA units is caused by the self-assembly process responsible for hydrocarbon close packing.

Key Words—2-dimensional Ordering, HDTMA-Br Salt Molecules, HDTMA-vermiculites, Interlayer Structure, Self Assembly, Swelling, Toluene.

INTRODUCTION

The expandable interlayer space of phyllosilicates, including that of smectites and vermiculites, can be used to organize intercalated organic cations and molecules. Organo cations exchange with indigenous inorganic cations and organic molecules either replace water molecules, associated with the silicate surfaces and hydrated inorganic cations, or they are sorbed by previously intercalated organic species (Slade *et al.*, 1978). The intercalation of organic components can not only enhance the organophilic character of clay minerals and make them useful sorbents for organo toxins, but they can also lead to ordered nanostructures in which reactants may be organized or adsorbed into matrices with specific geometric or chemical properties (Ogawa and Kuroda, 1995). Quaternary ammonium compounds, such as hexadecyltrimethylammonium (HDTMA) bromide, have frequently been used with clay-sized particles to produce organophilic intercalates. Lee and Kim (2002) showed that water-washed HDTMA-intercalated smectites contain co-adsorbed HDTMA-Br molecules, which could be removed by ethanol washing. Studies have shown that the configurations taken by the organic moieties in the interlayers of variously charged smectites influence the uptake of toxins (Slade and Gates, 2003), but details of their structures and modes of action are still uncertain (Theng, 1974; Lagaly, 1981; Favre and Lagaly, 1991; Xu and Boyd, 1995; Lee and Kim, 2002). In part, these uncertainties reflect the

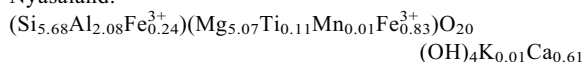
difficulty of obtaining suitable XRD data for structural studies on fine-grained, disordered smectites. However, large flakes of relatively well-ordered vermiculite are available and previous XRD studies of their intercalates have shown that their diffraction patterns may include extra reflections in the form of diffuse streaks and spots between the reflections given by the silicate layers. These extra reflections are associated with the interlayer structures and can provide important information about them (Alcover *et al.*, 1973; Raupach *et al.*, 1975; Slade *et al.*, 1978, 1998; Slade and Raupach, 1982; Slade and Stone, 1983). This study explores the use of powder and single-crystal XRD to reveal details of the interlayer structures in HDTMA cation-intercalated vermiculites, both with and without HDTMA-Br salt molecules. Changes that occur in these structures when toluene is sorbed are also considered.

EXPERIMENTAL

Materials and sample preparation

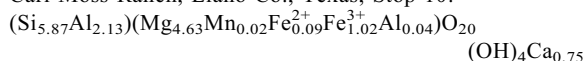
The two vermiculites of different charge used here were obtained from laboratory stocks originally analyzed, and reported on, by Norrish (1973). Their structural formulae, when Ca²⁺-saturated and ignited, are given as:

Nyasaland:



and

Carl Moss Ranch, Llano Co., Texas, Stop 10:



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Hence the Nyasaland vermiculite has a layer charge of 1.23 electrons per unit-cell (22 oxygen equivalents of charge) and the Llano Stop 10 vermiculite has a charge of 1.50 electrons. Portions of each material were cut into flakes $\sim 1\text{--}1.5$ mm across and then Na exchanged by refluxing them with fresh solutions (changed three times weekly) of 1 M NaCl at 45°C for 2 weeks. Flakes were then washed in warm deionized water until chloride was undetectable with AgNO_3 . After air drying, the Na-exchanged vermiculite flakes were reacted with a 0.01 M solution of HDTMA (Aldrich Chemical Company, Inc) under reflux at 45°C for 10 days; the reacting solution was changed periodically. Finally, the flakes were washed with distilled water to remove all leacheable HDTMA-Br salt. After air drying, their basal X-ray reflections were recorded when sets of rational spacings and sharp symmetrical reflections indicated that the exchange reactions were complete. Sub-samples of the water-washed flakes were then leached with ethanol by heating them under reflux at 45°C for 2 weeks. The ethanol was renewed periodically when the leachate was tested for bromide with AgNO_3 . The tests initially showed that further bromide was being released, but eventually it was no longer detectable. X-ray diffraction then demonstrated that a new set of sharp rational reflections, corresponding to a lower basal spacing, had developed.

X-ray diffraction techniques

The basal spacings of HDTMA-intercalated flakes, aligned on porous ceramic plates were recorded for $\text{CoK}\alpha$ radiation with a Philips PW1050/25 powder diffractometer fitted with a $1/12^\circ$ entrance slit and a 1° exit slit. Spacings resulting from liquid toluene uptake were obtained by allowing a toluene-moistened pad of cotton wool to press against the underside of the ceramic plates; wicking kept the flakes on the upper surfaces moist. Basal spacings for flakes in toluene vapor were recorded by ensuring that the toluene-moistened pad did not contact the ceramic plates. Measurements associated with both toluene liquid and toluene vapor were taken after specimens had equilibrated with the atmosphere in the closed specimen chamber.

Transmission XRD patterns of single, intercalated vermiculite flakes were obtained with filtered $\text{CoK}\alpha$ radiation by using either a 60 mm diameter Unicam single-crystal oscillation goniometer or a Huber Weissenberg goniometer with a 57.3 mm film cassette. The basal surfaces of flakes were maintained perpendicular to the incident X-ray beam, requiring the film cassette of the Weissenberg goniometer to be fixed and the oscillation mechanism of the Unicam camera to be disengaged. Patterns for flakes in toluene vapor were recorded while a stream of air, which had passed through toluene in a Drechsel bottle, was directed through a fine jet onto the specimen. The transmission patterns for flakes in liquid toluene were obtained from samples

supported in an annulus of blotting paper wet with toluene and sandwiched between Mylar windows kept taut by being stretched over the end of a tapered plastic sleeve inserted into a matching clamping sleeve.

RESULTS AND DISCUSSION

The basal spacings of water-washed, HDTMA-intercalated vermiculite flakes are: 29.3 Å for Nyasaland and 29.6 Å for Llano Stop 10; their transmission XRD patterns are indistinguishable, and are represented by Figure 1a. After the water-washed flakes had been leached in ethanol, their basal spacings had not only decreased to 26.3 Å and 25.8 Å, respectively, but their transmission diffraction patterns (Figure 1b) had also changed as can be seen by comparing Figures 1a and 1b. Slade and Stone (1983) pointed out that transmission diffraction patterns, such as those being considered here, result from the superpositioning of three basic components, each of which arises from a set of domains in which the interlayer structure is coherently ordered in two dimensions. The ordering within all domains is basically the same and for a set of domains, with a coherently ordered structure, a characteristic vector can be selected so that the corresponding vectors for the other two sets are rotated by $\pm 120^\circ$ with respect to the first vector. The diffraction pattern observed therefore represents the integration of the diffraction effects produced by all the sets of ordered domains traversed by the incident beam.

Figure 2 is a scaled representation of the reciprocal lattice planes corresponding to the diffraction photographs in Figure 1a and 1b; it shows both the reciprocal lattice points for the host vermiculite layers and the additional points associated with the intercalated HDTMA. For the water-washed flakes, the additional points occur in pairs equidistant from the origin, so that an individual member of a pair has a corresponding member $\pm 120^\circ$ away. The symmetry of the pattern associated with these points therefore is trigonal and does not show centrosymmetry. Since Friedel's Law requires the X-ray symmetry of the $\mathbf{a}^*\mathbf{b}^*$ plane to include a center, its absence here is a consequence of stacking disorder. This disorder causes the superlattice reflections to degenerate into rods along \mathbf{c}^* . The asymmetric modulation of these rods, projected back onto the $\mathbf{a}^*\mathbf{b}^*$ plane as they contact the Ewald sphere for upper reciprocal lattice layers, results in the loss of centrosymmetry. For flakes that had been water-washed initially and then ethanol-leached, a somewhat different reciprocal lattice occurs in which points no longer exist in pairs, but as single points. These have a reciprocal interval along the \mathbf{a}^* axis which is 1/3 of the original value and therefore relate to a superstructure with a unit-cell with an axis $3 \times$ that of the vermiculite itself. The reciprocal interval along \mathbf{b}^* is not subdivided and hence, the interlayer organic cations are ordered on a centered

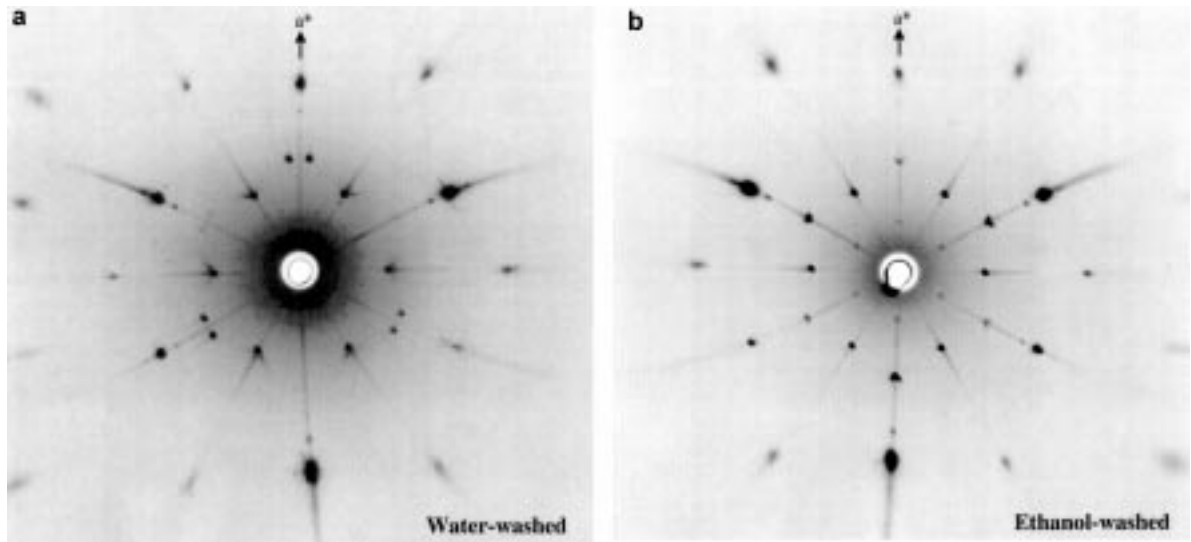


Figure 1. Transmission XRD image of (a) water-washed and (b) ethanol-washed HDTMA-exchanged vermiculite (CoK α radiation).

$3a \times b$ orthohexagonal superlattice that is equivalent to a hexagonal lattice based upon a unit-cell with axes of 9.18 Å (Henry and Lonsdale, 1969).

Figure 2 shows that the reflections paired in groups marked 1, 2 and 3, for water-washed HDTMA-vermiculite are slightly further from the origin than the nearby 400, $\bar{2}20$ and $\bar{2}\bar{2}0$ superlattice reflections (orthohexagonal indexing) for the alcohol-washed product. X-ray films taken of flakes at various stages of being alcohol-washed show that their paired reflections streak towards, and ultimately become, the 400, $\bar{2}20$ and $\bar{2}\bar{2}0$ reflections. The hexagonal cell of water-washed HDTMA-vermiculite is therefore both smaller and slightly rotated with respect to the hexagonal cell for the alcohol-washed

material. The differences are probably caused by changes to the orientations of the organic interlayer units as their packing density decreases, when HDTMA-Br molecules are removed with alcohol.

From the reflections in groups 1, 2 and 3, some basic information can be obtained. A given member of a pair and its equivalents at either $\pm 120^\circ$ correspond with sets of atomic planes which themselves intersect at $\pm 120^\circ$. Measurements show that these planes are 3.96 Å apart and, as seen in Figure 3, their intersections define a hexagonal cell for which the axes a and b can be calculated as 4.57 Å. The axis a is rotated by 1.86° from the a^* axis of the vermiculite host and this non-commensurate rotation can be expected to influence

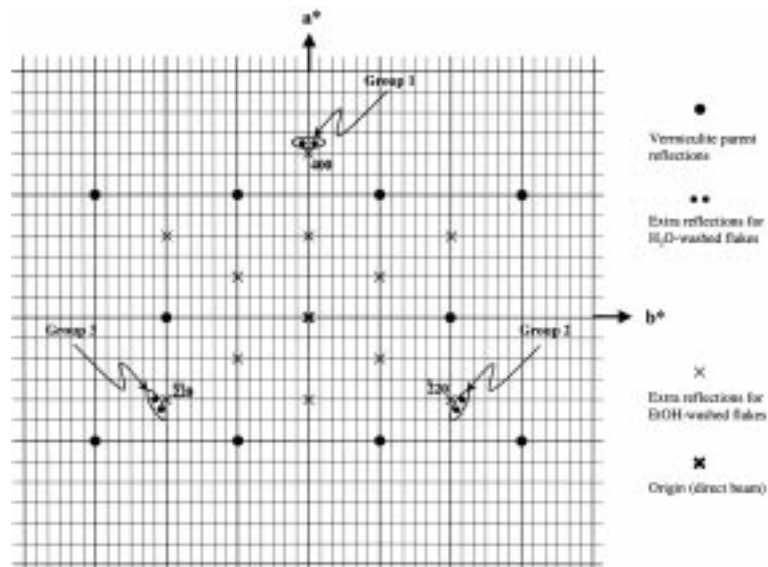


Figure 2. The diffraction patterns of water-washed and ethanol-washed HDTMA-vermiculites scaled to the vermiculite a^*b^* plane.

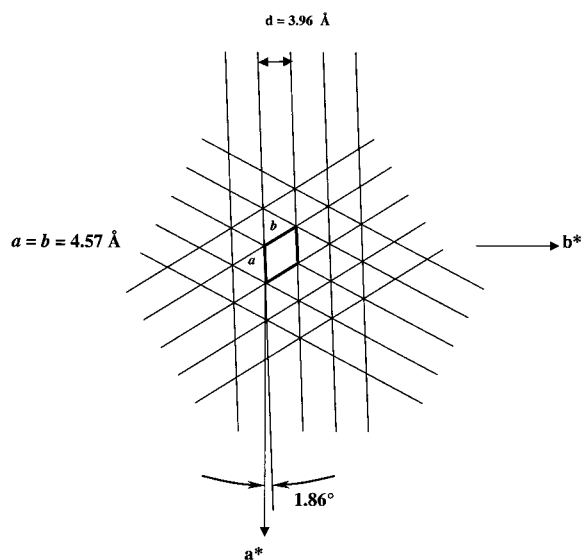


Figure 3. Sets of planes (120° apart) in HDTMA-vermiculite on which equivalent organic units are sited. Their spacings are 3.96 \AA and their intersections define a hexagonal sub-cell with axes of 4.57 \AA . For water-washed HDTMA-vermiculite, the sub-cell axes are rotated by 1.86° from a^* .

the size of the ordered domains. The interlayer structure of the water-washed material is therefore based upon a hexagonal subcell, which is close to half the size of that

for the ethanol-washed material. The smaller cell, and therefore the higher density of packing of the organic units in the interlayers of the water-washed intercalate, results from an organized association of HDTMA cations and HDTMA-Br molecules. When the HDTMA-Br molecules are removed with ethanol, the HDTMA cations remain in a less densely packed superstructure with the larger, true hexagonal unit-cell with axes of 9.18 \AA .

The relationship between the interlayers and the silicate surface

If the assumption is made that the charged head-groups of HDTMA cations engage with the ditrigonal cavities of the silicate surfaces (Slade and Stone, 1983, 1984), a scaled drawing of a surface can be over-ruled with traces of the reflecting planes on which the organic scattering units in water-washed HDTMA-vermiculite are positioned (Figure 4). These planes, with interplanar spacings of 3.96 \AA , will then pass alternately through the centers of ditrigonal cavities, or the oxygens shared between silica tetrahedra. Therefore, on a given silicate surface, the HDTMA cations occupy different sites to those occupied by the HDTMA-Br molecules; the resulting sub-cell, which accommodates both the organo salt molecules and cations, is marked DGHI in Figure 4. In comparison, the larger, true hexagonal (primitive) cell, corresponding to the diffraction pattern shown in

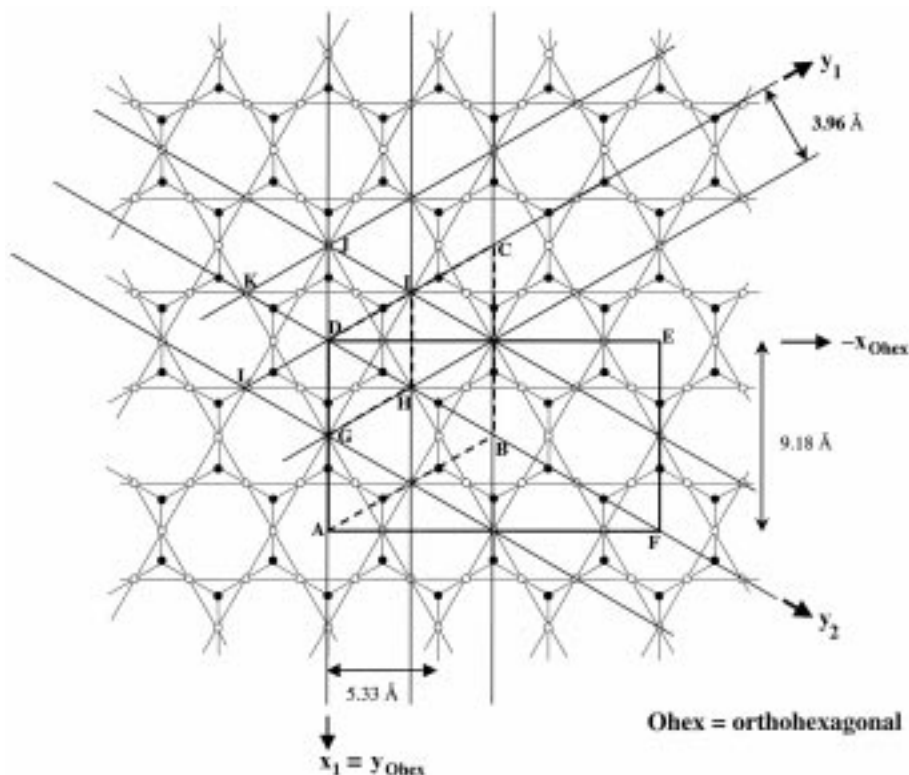


Figure 4. Schematic representation of the relationships between the silicate surface and planes of organic units. The hexagonal cell ABCD and the orthohexagonal cell ADEF of HDTMA-vermiculite are shown in relation to the smaller hexagonal cell DGHI.

Figure 1b for alcohol-washed HDTMA-vermiculite is that marked ABCD with sides of 9.18 \AA . Along these sides, the organic scattering units are organized in an *aba...* sequence which could correspond to HDTMA cations with their head groups alternately up and down. This arrangement allows two opposed silicate surfaces to each have cations attached that are organized on the larger hexagonal lattice so that their aliphatic tails interlock and form an alternating sequence. Scale models show that if a sequence of organic units is arranged with their aliphatic chains at $\sim 50^\circ$ to the silicate surface, head groups alternately up and down, zig-zags parallel and with CH_2 groups interlocked, a linear distance of $\sim 9 \text{ \AA}$ will be covered. This distance closely corresponds to the repeat distances along the x_1 , y_1 and y_2 axes (Figure 4).

Figure 5 shows a structural model for an ordered domain on a single surface of HDTMA-vermiculite. The HDTMA cations in the ethanol-washed material are positioned over the centers of the ditrigonal cavities and arranged in a hexagonal lattice; *i.e.* positions ABCD in Figure 4: the head groups are then either all up or all down. The intervening positions GHIJKL, over bridging oxygens, are available for occupation either by HDTMA cations or HDTMA-Br molecules with their head groups oriented opposite to those of the HDTMA cations on sites ABCD. Extra HDTMA cations will be required to balance layer charges above the value of $1.33 e^-$ per parent unit cell, which is the limiting charge resulting from the occupation of equivalent positions in the $3a \times b$ supercell. The basal spacing differences between the water and alcohol-washed Nyasaland and Stop 10 vermiculites, 3.00 and 3.87 \AA , respectively, indicate that an offset exists between the HDTMA cations and the HDTMA-Br molecules. This offset allows the large

bromide anion, with its radius of 1.95 \AA , to be incorporated (Figure 6).

The effects of toluene sorption

The basal spacings of alcohol-washed HDTMA-vermiculites equilibrated with toluene vapor are $\sim 36 \text{ \AA}$ and their transmission diffraction patterns are the same as that previously observed for alcohol-washed flakes (Figure 1b), and therefore they retain their 2-dimensional ordering on the silicate surfaces. However, in liquid toluene, flakes have a basal spacing of 44.7 \AA but their transmission diffraction patterns do not include any superlattice reflections; only parent silicate reflections are present. After flakes have been in liquid toluene and heated for 2 h at 60°C , to remove all sorbed toluene, their basal spacings returned to $\sim 26 \text{ \AA}$. Although this value is the same as that given by HDTMA-Br free, alcohol-washed HDTMA-vermiculite, the transmission diffraction pattern is the same as that given by water-washed, HDTMA-Br-containing flakes (Figure 1a).

The diffraction effects produced by toluene in alcohol-washed HDTMA-vermiculite can be explained as follows. The expansion of the basal spacing of HDTMA-vermiculite in toluene vapor (from ~ 26 to $\sim 36 \text{ \AA}$) is insufficient to effectively remove the overlap of the aliphatic portions of HDTMA cations attached to opposed silicate layers (Figure 7a). Consequently, the ordered relationship between the silicate layers with their attached organic cations remains undisturbed. However, in liquid toluene the interlayer spacing increases to 44.7 \AA so that the aliphatic chains no longer overlap (Figure 7b). This leads to the loss of their ordered distribution as seen by the disappearance of superlattice reflections. When sorbed toluene is driven

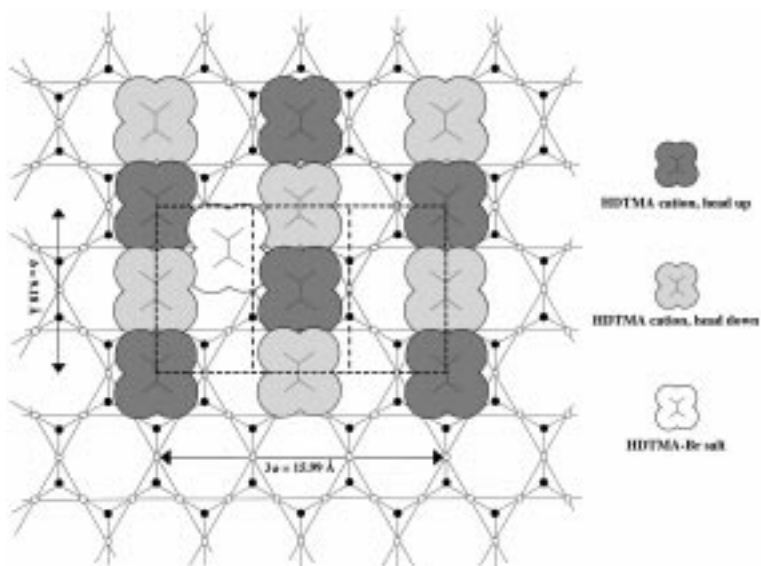


Figure 5. The interlayer structure of HDTMA-vermiculite showing cation and salt positions. The planes containing the zig-zag carbon chains may be $\pm 120^\circ$ from the orientation given.

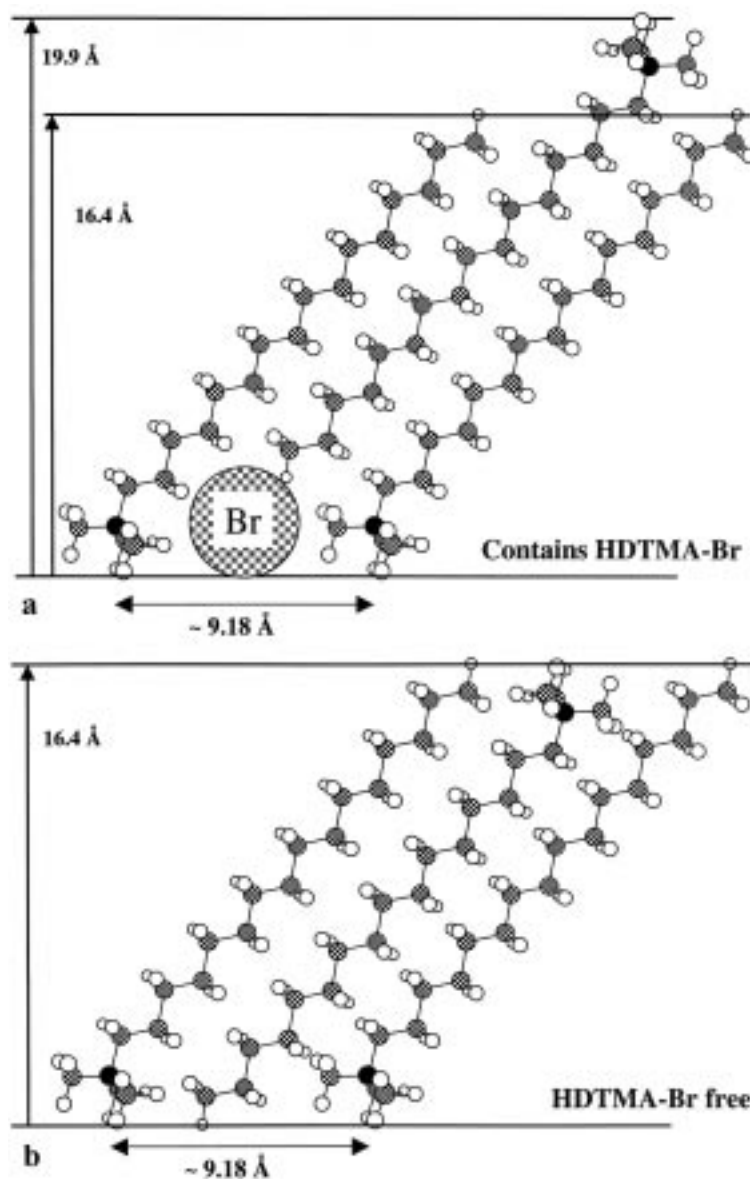


Figure 6. Schematic representation of (a) water-washed and (b) ethanol-washed HDTMA-vermiculite. Vertical arrows indicate free space (basal spacing of 9.6 Å) between silicate layers. Horizontal arrows indicate distance between equivalent repeating organic units on the silicate surface.

off, the organic cations again overlap and, taken over the crystal as a whole, occupy any of the available ABCD or GHIJK sites (Figure 4) provided adjacent cations always have their head groups alternating up and down. A close-packed structure similar to that in the water-washed, HDTMA-Br-containing structure results. Transmission diffraction patterns of flakes, which have been purged of liquid toluene as described and then steeped in alcohol, once again show the distribution of extra reflections illustrated in Figure 1b. Here, alcohol is not removing HDTMA-Br, but instead it breaks the van der Waals attractions binding the aliphatic chains and allows them to order in a lower energy, less densely-packed, structure

based upon the primitive hexagonal cell ABCD. Sites at the centers of these cells (site H in Figure 4) will be vacant unless they are partially occupied to balance excess layer charge. The enhanced swelling of HDTMA-vermiculite flakes (and other organo-clays) in toluene and alcohol (Slade and Gates, 2003) is dependent on the abilities of these solvents to overcome the van der Waals forces operating between aliphatic chains of organic cations attached to adjacent silicate surfaces.

The extensive swelling which liquid toluene induces in HDTMA-vermiculites destroys its ordered interlayer structure. If the organic counter ions were strongly electrostatically associated, on a one-to-one basis, with

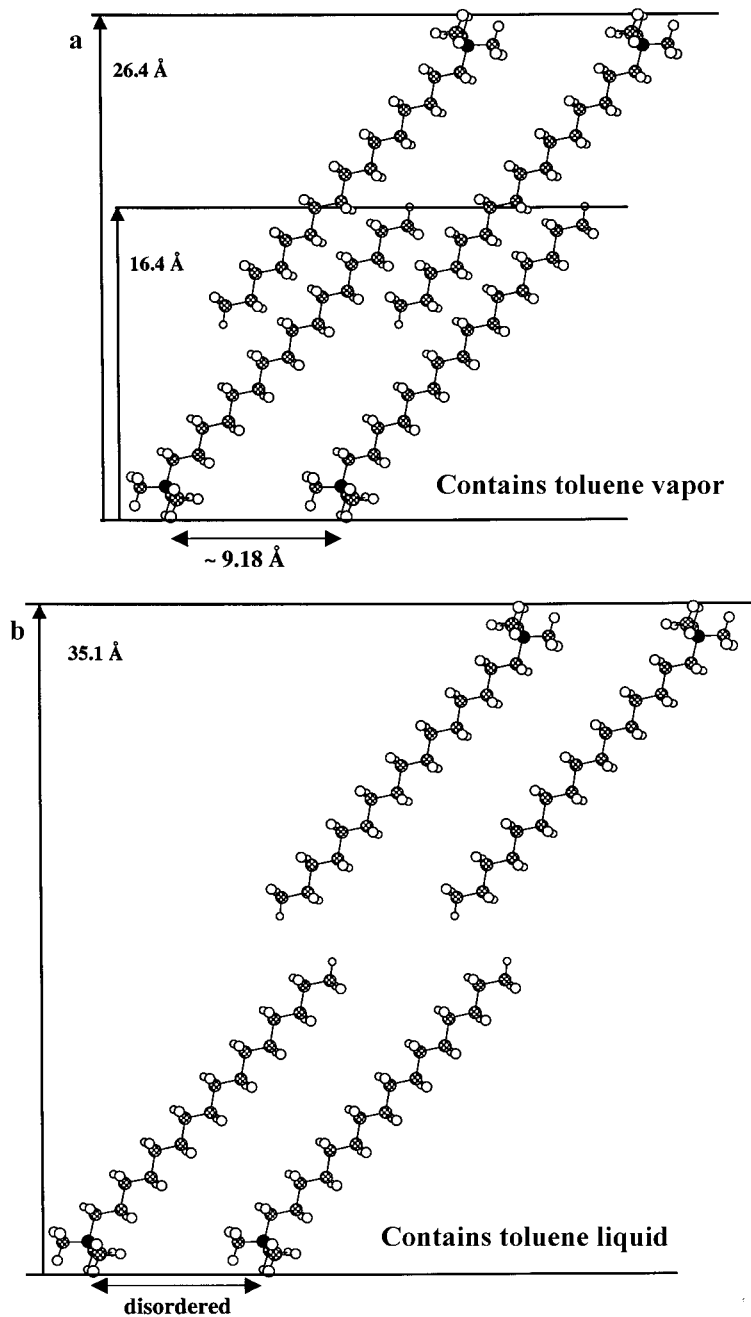


Figure 7. Schematic representation of HDTMA-vermiculite solvated with (a) toluene vapor and (b) toluene liquid. Vertical arrows indicate free space (basal spacing of 9.6 Å) between silicate layers. Horizontal arrow in (a) indicates the repeat distance between equivalent organic units on the silicate surface. In (b) this distance is not fixed.

correspondingly ordered surface charges, the 2-dimensional ordering of cations on opposing silicate surfaces would possibly persist after swelling. However, if the negative layer charge is diffused over the surface, or is randomly distributed, the ordering of the organo cation will be controlled by steric factors and van der Waals forces operating between them. These determinants lead to the interdigitation of aliphatic chains and the *aba...*

packing with its ~ 9 Å repeat, discussed above. On the silicate surfaces, along the x_1 , y_1 and y_2 directions (Figure 4), this repeat distance coincides with the distance between rings of surface oxygens, and allows the organic and silicate layers to intermesh. The superstructure reflections, seen in the transmission patterns, result from the coherent diffraction produced by this intermeshing. Toluene, with its capacity to weaken the

van der Waals forces between close-packed hydrocarbon chains, and possibly bind to them directly via these forces, leads to the disordering of the interlayer structure. Conversely, as toluene evaporates and the interlayer spacing falls, hydrocarbon chains reform into closely packed arrays. Thus, the factors responsible for hydrocarbon chains forming closely packed structures override the electrostatic forces operating between the organic cations and the silicate layers. The extent to which this structure is occupied by cations is determined by the layer charge of the vermiculite. For the two vermiculites used in this study, the layer charges, and consequently the cation occupancies, are sufficiently close that their diffraction patterns are the same, but more highly charged vermiculites might give different results due to higher packing densities required.

CONCLUSIONS

This XRD study of HDTMA-intercalated vermiculites has shown that when they contain HDTMA-Br salt molecules, they have a basal spacing and a transmission diffraction pattern which differ from those of their HDTMA-Br free (ethanol-washed) counterparts. On a single silicate surface, the interlayer HDTMA cations are arranged on a $3a \times b$ superlattice which allows some additional HDTMA cations and HDTMA-Br molecules to be incorporated. This arrangement has the head groups for adjacent organic units directed alternately up and down. The ordered 2-dimensional arrays persist during swelling in toluene vapor, but disappear in toluene liquid. The transmission XRD patterns of HDTMA-vermiculites indicate that in toluene vapor, the aliphatic chains of the organic cations remain interdigitated; however, in toluene liquid, the extent of interlayer swelling is sufficient to overcome the interdigitation and disorder results. The self-assembly of quaternary ammonium units within interlayers is responsible for the 2-dimensional ordering.

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