HDTMA IN THE INTERLAYERS OF HIGH-CHARGED LLANO VERMICULITE

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Abstract—X-ray diffraction shows that ordered interlayer structures form when high-charged Llano vermiculite is reacted with HDTMA-Br or HDTMA-acetate, but the structures differ from those given by low-charged vermiculites. The differences arise in two ways; firstly when both HDTMA$^+$ cations and HDTMA-Br (or -acetate) ion pairs are present as interlayer guest species, a superstructure forms which is less commensurate with the host structure of high-charge vermiculite than it is for lower-charged material. Secondly, although a commensurate $3a \times b$ interlayer superstructure forms when HDTMA$^+$ cations are the only interlayer guests, an increasing number of charge-balancing cations must be accommodated as the layer charge increases. This results in some structural disorder which is only observed in the diffraction pattern of HDTMA$^+$-intercalated, high-charge vermiculite. Organic ion pairs tend to order along widely spaced rows corresponding to the intersections of two sets of scattering planes. For the acetate form, one set of planes has spacings of 3.52 Å, but for the bromide form the value is 3.67 Å. Scattering planes in the second set have spacings of 4.02 Å, independently of counter-anion size. These two sets of planes diverge from one another by ~10°. Ordering is more apparent in the presence of acetate anions than it is for the smaller Br$^-$ anions. In the high-charged intercalates, from which organic ion pairs have been removed, HDTMA$^+$ cations occupy positions on a centered two-dimensional superlattice and also randomly, some interstitial positions as necessitated by layer charge.

Key Words——HDTMA-acetate Molecules, HDTMA-vermiculites, High-charge Vermiculite, Interlayer Structure, Two-dimensional Ordering, Structural Models.

INTRODUCTION

X-ray diffraction (XRD) studies of vermiculites have shown that their diffraction patterns may include diffuse streaks and spots between the reflections associated with the silicate layers. This has been reported by Alcover *et al.* (1973), Raupach *et al.* (1974), Slade *et al.* (1978), Slade and Raupach (1982), Slade and Stone (1983), Slade *et al.* (1998) and by Slade and Gates (2004). Diffuse streaks have also been observed in the XRD patterns of muscovite (Gatineau, 1964). Similar reflections have been seen in the electron-diffraction patterns of pyrophyllite and talc (Kodama, 1975), of beidellite (Güven and Pease, 1975) and also of muscovite associated with vermiculitized products (Kodama, 1977). In altered muscovite, the diffuse streaks have been attributed by Kodama (1977) to 'structural disturbances'. In vermiculites however, the extra spots and diffuse streaks are more usually associated with interlayer cations and water molecules which are ordered to varying degrees within two-dimensional domains (Slade *et al.*, 1998). The sizes of such domains are limited to different degrees in specific directions and the extensions of the diffuse streaks are reciprocally related to the domain sizes.

An important aspect of the limited size of these ordered domains is demonstrated by the extra reflections seen as spots on the $a*b*$ reciprocal lattice planes of intercalated vermiculite. In the $c*$ direction these reflections extend as rods that intersect successive reciprocal lattice layers on which they appear as spots. Therefore, the domains are only ordered coherently in two dimensions on the basal surfaces of the silicate layers; the ordering does not extend from layer to layer. The width (D) of a coherent ordered domain is related to the rod (spot) diameter by $D \approx \lambda\beta\cos\theta$ where λ is the half-maximum diameter of a spot in radians (Klug and Alexander, 1954, 1974).

The presence of sharp, extra spots, as for example observed in the $a*b*$ planes of cetylpyridinium bromide-intercalated vermiculite (Slade *et al.*, 1978) or La^{3+}-vermiculite (Slade *et al.*, 1998), shows that interlayer species can form ordered superstructure arrays on the basal surfaces of the silicate layers. However, extra spots, *e.g.* as observed in the XRD image of the $a*b*$ plane of benzidine- or aniline-vermiculite intercalates (Slade and Raupach, 1982, Slade and Stone, 1984, respectively), may not arise from the presence of a superstructure, but instead they may occur because the symmetry of the organic interlayers is less than that of the host structure.

Extra reflections resulting from a high degree of interlayer ordering are potentially especially valuable where the absence of full long-range order in three dimensions precludes complete structural analysis. For vermiculites, large flakes suitable for single crystal X-ray

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studies are available, but after intercalation many of these remain structurally disordered. Nevertheless, valuable information about interlayer ordering can be obtained from them if superlattice reflections are present. Such information may be helpful in the development and study of self-assembling nano-structures having specific geometrical or chemical properties.

Recently, X-ray data of this kind were used by Slade and Gates (2004) to study the organization of hexadecyltrimethylammonium bromide (HDTMA-Br) intercalated into vermiculites with low to moderate layer charges (1.25 to 1.5 e^- per 22 oxygen equivalents). These intercalates, if formed in an aqueous solution of HDTMA-Br, contained charge-balancing organic cations (HDTMA$^+$) and also co-adsorbed HDTMA-Br ion pairs. The latter were removed by leaching with ethanol, leaving only HDTMA$^+$ counter ions in the interlayers. X-ray diffraction showed that intercalates either with or without entrained ion pairs have ordered, but different, two-dimensional interlayer structures. In the ion pair-free structure, the cations are arranged within the interlayers on a $3a \times b$ superstructure, with respect to the orthohexagonal cell of the parent vermiculite. This allows sequences of HDTMA$^+$ cations to form with their head-groups pointing alternately up and down along the rows containing the zigzag planes of the aliphatic chains. The aliphatic tail axes are parallel to one another, but also inclined at ~50º to the silicate surfaces (Brovelli *et al*., 1999). The superstructure enables opposed interlayer surfaces to have cations attached in a formation based upon an equivalent hexagonal cell with sides of ~9.2 Å. When the HDTMA-Br ion pair molecules are also entrained, they occupy sites along rows intermediate between those which define the 9.2 Å hexagonal cell (Slade and Gates, 2004).

The work of Slade and Gates (2004) revealed that host-guest and guest-guest interactions strongly influence the two-dimensional self-assembled superstructures formed. The guest-guest interactions are dominated by van der Waals forces operating between the aliphatic tails of adjacent HDTMA$^+$ and HDTMA-Br ion pairs, and give rise to superstructures which are largely incommensurate with the parent vermiculite structure. On the other hand, host-guest interactions are dominated by the electrostatic attraction between the organic cations and the interlayer surface. With the lower packing density associated with intercalates containing only organic cations, superstructures are produced that are more commensurate with the host structure.

On a single silicate interlayer surface, a two-dimensional centered $3a \times b$ super-cell occupied by two asymmetric units of HDTMA$^+$ cations, each carrying a single positive charge can, in combination with a similar arrangement on an adjacent surface, balance an ideal total charge of 1.33 e^- per standard three-dimensional unit-cell of vermiculite. However, greater layer charges require additional cations to occupy additional sites

within the super-cell. The highest-charged vermiculite used by Slade and Gates (2004) carried a charge of 1.5 e^- and so ~1 additional HDTMA$^+$ cation, per two super-cells, was needed for charge neutrality. This relatively low population of additional cations was insufficient to modify the transmission XRD patterns enough for them to differ from those given by the intercalate formed with the lowest-charged vermiculite. The work reported here, however, shows that the transmission XRD patterns for HDTMA-Br or HDTMA-acetate intercalated higher-charged vermiculites differ considerably from those for similarly intercalated lower-charged vermiculites.

The present paper considers intercalates formed by a vermiculite from Llano County, Texas. This material has the highest known charge (~1.9 e^- per unit-cell) for a vermiculite, and thus seemed capable of producing the maximum degree of incommensurate character of the resulting superstructures. The intercalants used were HDTMA-Br and HDTMA-CH$_3$COO, the acetate anion being used to ascertain how a larger anion might influence the two-dimensional arrays formed within the interlayer spaces.

EXPERIMENTAL

Materials and sample preparation

The high-charged vermiculite used here was collected by K. Norrish from the Carl Moss Ranch, Llano County, Texas, USA and was obtained from the reference collection held in CSIRO Land and Water. It is designated as Stop 12 and was analyzed by Norrish (1973) who reported its structural formula on the basis of 22 oxygen equivalents per unit-cell (ignited) and Ca^{2+}-saturated as: $(Si_{5.79}Al_{2.21})(Mg_{5.62}Ti_{0.04}$ $Mn_{0.01}Fe^{3+}_{0.13}Al_{0.16})O_{20}(OH)_4K^+_{0.03}Ca^{2+}_{0.93}$.

The effective layer charge is therefore ~1.90 electrons per standard unit-cell comprising 22 oxygen equivalents of charge. For the current work, selected portions of the material were cut into flakes ~1−1.5 mm across and initially Na$^+$ exchanged by the method described in Slade and Gates (2004). After being air dried, the Na$^+$-exchanged flakes were reacted at 45ºC for 10 days with either 0.01 M solution of HDTMA-Br (Aldrich) or HDTMA-acetate (obtained from the bromide form by ion exchange using a Dowex 1×8, 50−100 mesh resin in acetate form). The reacting solutions were changed every second day. Leachable organic ion pairs were removed by washing the products with warm distilled water and, when the flakes were air dry, their basal X-ray reflections were recorded. Sets of rational, sharp and symmetrical reflections were indicative of complete exchange. Samples of the water-washed flakes were also leached with ethanol by heating them under reflux for 2 weeks. The ethanol was renewed at intervals when the leachate from the HDTMA-Br treated flakes was tested for Br$^-$ with silver nitrate. As this test

was unsuitable for the HDTMA-acetate treated flakes, XRD was again employed to ensure that both materials gave similar sets of rational sharp reflections corresponding to a lower spacing than that given by the ion pair-containing materials.

XRD techniques

The methods used to obtain basal spacings and transmission XRD patterns were given by Slade and Gates (2004). Since the transmission diffraction patterns for the HDTMA-acetate intercalate were especially sharp, but also distorted as a result of a reciprocal plane being projected onto a cylindrical surface, precession photographs, taken with MoKα radiation, were also made for this material. The precession photographs enabled the geometrical parameters of the non-parent reflections to be measured as accurately as possible.

RESULTS AND DISCUSSION

The basal spacing of water-washed Llano Stop 12 vermiculite, intercalated with HDTMA-Br, is 31.0 Å and with HDTMA-acetate, is 29.9 Å. After the intercalates had been leached with ethanol, their basal spacings changed to 26.0 and 26.5 Å, respectively. The basal spacing of high-charged HDTMA vermiculite is therefore essentially the same as for the low-charged materials (Slade and Gates, 2004). The transmission XRD patterns of the water-washed materials differ as shown in Figures 1a and 1b. In particular, the pattern for the HDTMA-Br intercalate (Figure 1a) shows a set of non-vermiculite reflections (arrowed) the members of which are weaker and more streaked than the equivalent reflections in the pattern for the HDTMA-acetate intercalate (Figure 1b). The transmission diffraction patterns of the ethanol-leached materials are similar for both high- and low-charge intercalates and are represented by Figure 1c. To emphasize an important difference between the diffraction patterns of low- and high-charged intercalates, Figure 2 (from Slade and Gates, 2004) is modified here to include the arrowed reflections seen in Figures 1a and 1b. These reflections are only given by the high-charge intercalates. The diffraction photographs of all water-washed intercalates show groups of fairly sharp, non-vermiculite reflections (labeled groups 1, 2 and 3 in Figure 2), but the reciprocal-space parameters for these reflections differ between samples.

Ethanol washing destroys the above mentioned non-vermiculite reflections in both the low- and high-charged vermiculites, and they are replaced with reflections (Figures 1c and 2) associated with a $3a \times b$ superstructure on the orthohexagonal unit-cell of vermiculite. For the high-charged intercalate, Figure 1c shows that the superlattice reflections, corresponding to those indexed as 400, $\bar{2}20$ and the $\bar{2}\bar{2}0$ in Figure 2 still have associated streaks; these are absent for the corresponding reflections given by the ethanol-washed, low-charged intercalates.

The interplanar distance corresponding to the reflections in groups 1, 2 and 3 given by the HDTMA-Br intercalates formed using the low-charged vermiculites is 3.96 Å; the corresponding distance for the reflections similarly grouped and given by the HDTMA-Br intercalated high-charge vermiculite is 3.67 Å. For the HDTMA-acetate intercalate the distance is 3.52 Å. The streaked non-vermiculite reflections seen in Figure 1a were difficult to measure, but for the HDTMA-acetate intercalated high-charge vermiculite the corresponding reflections (Figure 1b) are sharp and result from an interplanar spacing of 4.02 Å.

The reciprocal vectors corresponding to the reflections in groups 1, 2 and 3, observed in all water-washed intercalates, do not coincide with an axial direction of the parent vermiculite, but are rotated from *a* as follows: low-charged HDTMA-Br intercalate, 1.86º (Slade and Gates, 2004); high-charged HDTMA-Br and HDTMA-acetate intercalates, 5.7±0.5º (Figure 3). For the arrowed, sharp, non-vermiculite reflections seen in Figure 1b, the reciprocal vector is rotated by 14.7±1.0º from *a*.

Possible models

Potentially, the 3.52 Å reflections could have resulted from scattering by organic units with their aliphatic zigzag planes parallel and tightly packed within rows separated by this distance. The ion pairs could then be posited as being on the 4.02 Å planes. However, this model does not account for the 3.52 Å reflections being considerably weaker than the 4.02 Å reflections, or for the fact that the intercalate structure accommodates more cations than ion pairs. A more satisfactory model results by considering a scale drawing (Figure 3) of the sets of the 3.52 Å and the 4.02 Å scattering planes. These planes are drawn at 6º (y_{11}) and 16º (y_{21}), respectively, to the direction of the *a* axis and their interplanar spacings are scaled to the length (5.33 Å) of this axis for vermiculite. As reflections have equivalents at either ±120º from them (Figures 1a and 1b), corresponding sets of planes could also be shown in Figure 3; however, for clarity, only one for each set is included. In combination, these planes define two separate sets of hexagonal cells: one set of cells having axes of 4.64 Å and the other set consisting of cells having axes of 4.06 Å. From Figure 3, the 3.52 Å and the 4.02 Å scattering planes are seen to intersect along rows which are 16.08 Å (4×4.02 Å), or ~15.99 Å (3×5.33 Å) apart. At specific positions along these rows, the corners of hexagonal cells from the separate sets nearly coincide and these positions are seen to form a coarse hexagonal array based upon a larger cell with axes of 18.56 Å (4×4.64 Å) $\approx$ 18.36 Å (2×9.18 Å), where 9.18 Å is the length of the *b* axis for vermiculite.

Further development of a structural model consistent with the geometry of Figure 3 follows Slade and Gates (2004) who considered that the aliphatic chains in low-
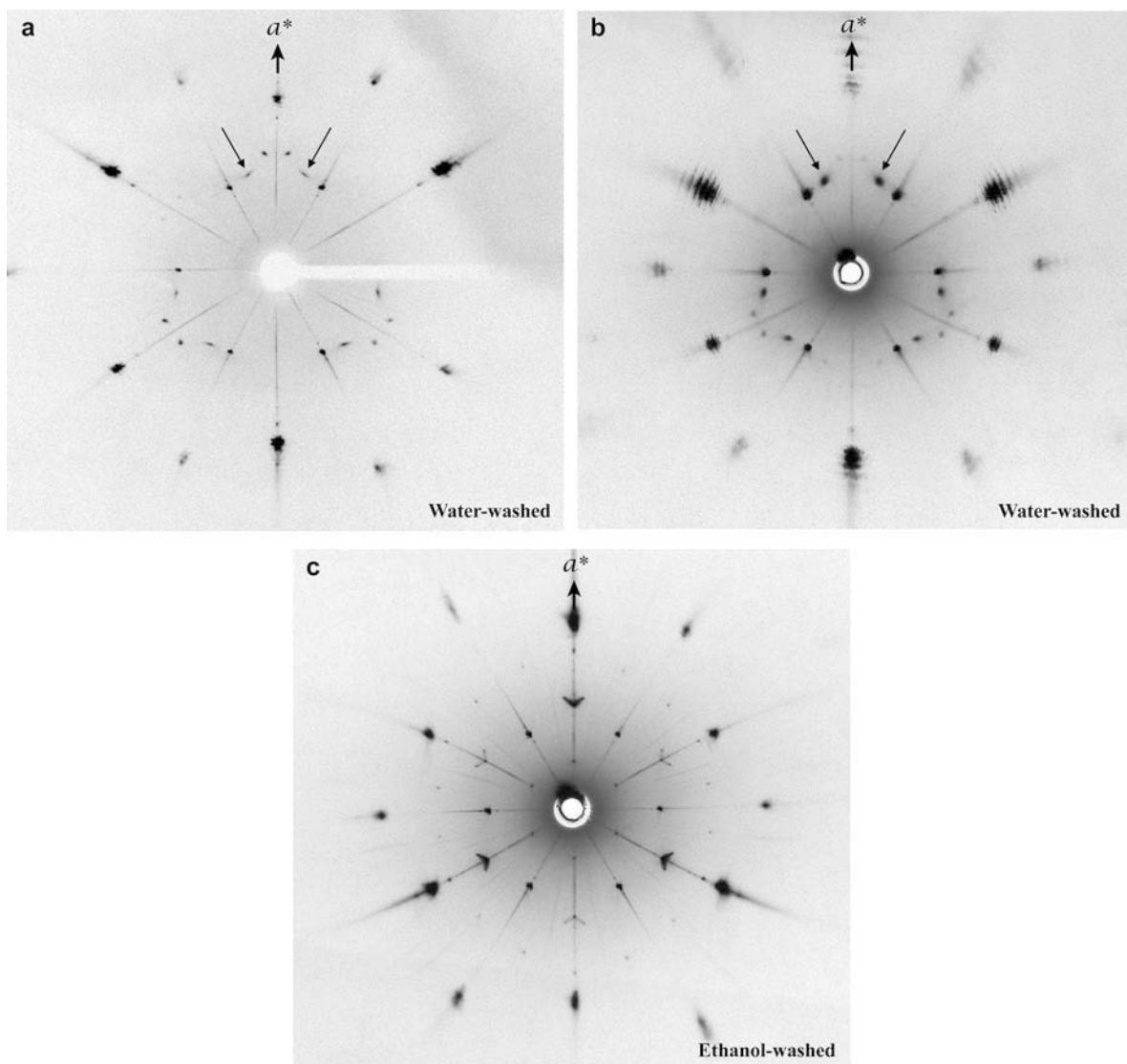
Figure 1. (a) Transmission XRD photo of water-washed Llano Stop 12 HDTMA-Br intercalate having HDTMA-Br ion pairs in excess of the vermiculite surface charge (CoKα). (b) Transmission XRD photo of water-washed Llano Stop 12 HDTMA-acetate intercalate having HDTMA-acetate ion pairs in excess of the vermiculite surface charge (CoKα). (c) Transmission XRD photo of ethanol-washed Llano Stop 12 HDTMA intercalate without HDTMA-(Br, acetate) ion pairs (CoKα).

charged HDTMA-vermiculite intercalate are also arranged in rows. Within the rows, chain axes rise at ~50° to the interlayer silicate surfaces, the HDTMA head-groups alternate between pointing up from and down to the surfaces, and the zigzag planes of the aliphatic chains are parallel to, and within, the rows. This arrangement results in a repeat distance of ~9.2 Å along a row and so is close to twice the axial length (2 × 4.64 Å) of the larger hexagonal cell mentioned above.

Furthermore, Slade and Gates (2004) reported that the interlayer structure of water-washed, low-charge HDTMA intercalates was based on a hexagonal sub-cell with axes of 4.57 Å. A similar approach here, of placing the chain axes at the corners of the larger (4.64 Å)

hexagonal cell enabled an array of organic scattering units (Figure 4) to be added to the geometric framework shown in Figure 3. As can be seen, the number of scattering units on the 3.52 Å planes is considerably less than on the 4.02 Å planes, which agrees with the experimental data showing that the 3.52 Å reflections are weaker than the 4.02 Å reflections.

Positions of ion pairs

The positions in the array (Figure 4) that are potentially available to ion pairs occur where the 3.52 Å and the 4.02 Å planes converge (Figure 3). As these convergences are on parallel rows, separated by 16.08 Å (4 × 4.02 Å), scattering from them could gen-

Figure 2. Transcription of the transmission XRD patterns of water-washed and ethanol-washed low-/intermediate-charged HDTMA-Br vermiculite intercalate scaled to the vermiculite *ab* plane (from Slade and Gates (2004), but showing here the high-charge vermiculite intercalate reflections (which are marked by arrows in Figures 1a and 1b).

erate a 16 Å reflection. Since out-of-plane scattering from the more heavily populated intermediate rows of cations will suppress the 16 Å scattering, these reflections will be absent in the water-washed materials. HDTMA ion pairs are arrayed along rows at the convergences of the 3.52 Å and the 4.02 Å planes.

Effect of alcohol washing

The transmission diffraction patterns of alcohol-leached flakes do not show either the 4.02 Å or the 3.52 Å reflections; they are replaced by the new set of non-host lattice reflections seen in Figure 1c. These reflections correspond to a C-face-centered superstructure with the dimensions of $3a \times b$ with respect to the orthohexagonal unit-cell of vermiculite ($a = 5.33$ Å and $b = 9.18$ Å). The new unit-cell has its axes parallel to those of the parent vermiculite cell and hence the development of the ion pair-free structure involves some repositioning of the organic cations on the silicate substrate. The rows of cations retain their 4.02 Å spacing but rotate from their original positions by ~16º to become

perpendicular to the *a* axis of the vermiculite. As noted earlier, the ion pair-free structure has a smaller interlayer spacing than that containing HDTMA ion pairs.

Effect of layer charge

As discussed above, the total negative charge (5.57 e$^-$) associated with three sub-cells of the high-charged vermiculite will be balanced if an average three-dimensional super-cell contains approximately six cations; three with their head-groups pointing down towards one vermiculite interlayer surface and three with their head-groups pointing up towards the opposing interlayer surface. The two-dimensional super-cell on a single interlayer surface outlined in Figure 4 satisfies this requirement if one of the four sites C, D, E or F (*e.g.* D) is occupied by a cation with its head-group directed towards the same silicate surface as the corner and C-face-centering cations. Thus, any one of the remaining three positions (*i.e.* C in Figure 4) must contain a cation with its head-group directed to the opposite silicate surface, leaving the other two sites (in this case, E
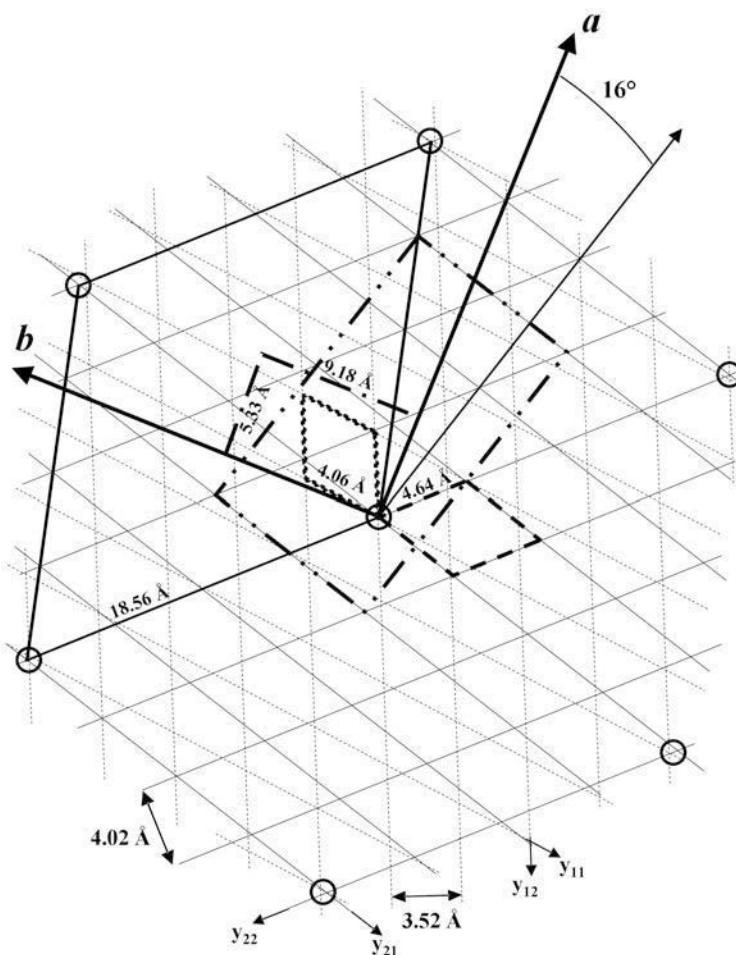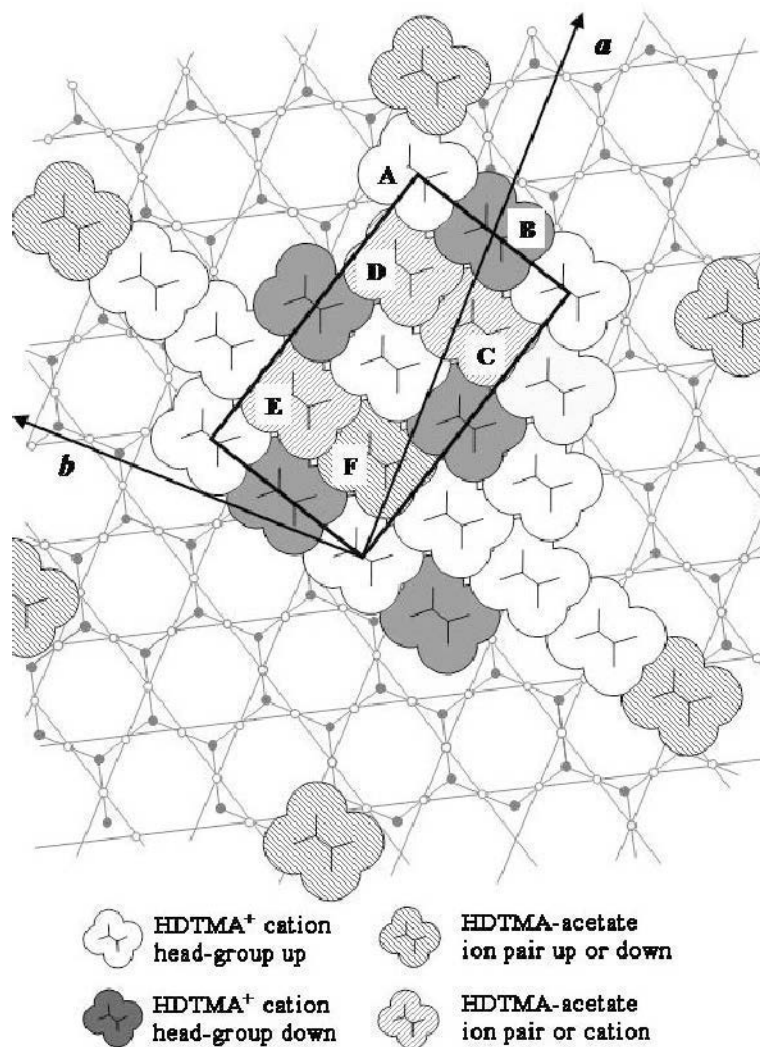
Figure 4. The proposed interlayer structure of a domain of Llano Stop 12 vermiculite intercalates containing HDTMA-acetate ion pairs. Sites A and B are sites of HDTMA$^+$ cations attached to adjacent surfaces, and thus along a row of such sites, head-groups point alternately up and down. Sites C, D and E are statistically filled with either additional HDTMA$^+$ cations or HDTMA-acetate ion pairs. The planes containing the zig-zag carbon chains of the aliphatic tails are rotated by 16º from the *b* axis of the host lattice. In other domains, this structure may be ±120º from the orientation shown. The aliphatic tails rise by ~50º with respect to the silicate interlayer surface.

results in a $3a \times b$ distribution which is largely commensurate with the host surface (Figure 5). The structure is further modified by such additional cations as are needed to maintain charge neutrality. These cations apparently statistically occupy available sites such as K, L and M in Figure 5 and the resulting disorder is responsible for streaking of the 400, $\bar{2}20$ and the $\bar{2}\bar{2}0$ reflections in the alcohol-leached, HDTMA$^+$-intercalated, high-charged vermiculite.

The structure proposed in Figure 5 allows a maximum charge of 2 e$^-$ per three-dimensional sub-cell of vermiculite to be balanced. This charge is slightly above the value for the vermiculite used here. Intercalates in, for example, a mica would probably adopt a different structure to that shown in Figure 5. The structures proposed here in Figures 4 and 5 seem to offer a basis for molecular modeling experiments such as those carried out by Čapková *et al.* (2006).

CONCLUSIONS

X-ray diffraction shows that intercalates formed by high-charged vermiculites and HDTMA cations, either with or without co-adsorbed ion pairs, while similar to the corresponding structures formed by low-charged vermiculite, show some important differences. When ion pairs are co-adsorbed, the differences are attributable to the incommensurate relationship between the host lattice
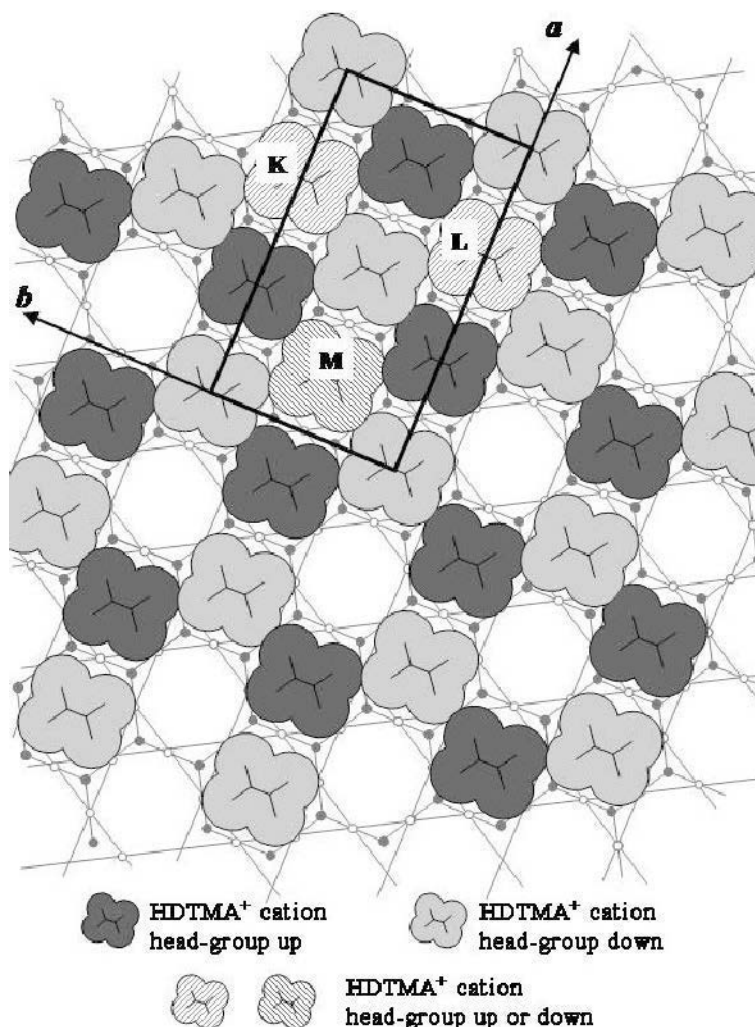
Figure 5. Proposed structure for the HDTMA[+]-intercalated high-charge Llano (stop 12) vermiculite. Sites K and L must contain HDTMA[+] cations with head-groups directed towards the same silicate surface, while a cation in site M has its head-group directed towards the opposite surface.

and the tightly packed guest lattice. In the ion pair-free structure of high-charge vermiculite, the majority of cations are arranged in a $3a \times b$ superstructure, but some additional cations needed for charge neutrality are disordered on available sites. The degree to which the fully loaded, ion pair-bearing guest and host structures are incommensurate increases with the increasing layer charge of the host.

In high-charged vermiculite containing co-adsorbed HDTMA-acetate, the ion pair molecules are ordered along parallel rows ~16 Å apart. Such ordering, although present, is less marked in the corresponding intercalate containing the less bulky HDTMA-Br.

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