REVISION 1

Interlayer water molecules in organocation-exchanged vermiculite and montmorillonite: A case study of tetramethylammonium

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ABSTRACT

Organoclays, unlike natural clays with inorganic cations that often have a hydration shell of H2O molecules, become organophilic and less adsorptive of H2O. These clays, therefore, are potentially important to remove organic contaminants from water; they are of great interest in industry for herbicide manufacture and as the basis for nanocomposite development; and they are of general interest in agriculture and in understanding soils. However, nothing is known about the positions of H2O in the interlayer when these molecules intercalate along with medium-sized hydrocarbon molecules, such as tetramethylammonium (TMA) cations. Even the positions of the TMA cations in the interlayer have been questioned recently. To resolve these issues, the orientation and
position of TMA and H$_2$O in the interlayer of vermiculite and montmorillonite were investigated by using atomistic computational methods. Interlayer H$_2$O content, layer charge, and location of layer charge were considered. For both vermiculite and montmorillonite and where the number of H$_2$O molecules is sufficient, TMA cations are located alternating between two planes in the interlayer. Each TMA cation is located near a tetrahedral-ring cavity of a 2:1 layer bordering the interlayer, and the H$_2$O molecules are disordered. In the absence of H$_2$O, TMA cations occur in one plane at the center of the interlayer. The major difference between vermiculite and montmorillonite is that the center of the TMA molecule in montmorillonite is 0.87 Å from the center of the interlayer as compared to 1.22 Å in vermiculite. Thus, the TMA cation is located closer to the tetrahedral-ring cavity in vermiculite, and this is a result of the greater tetrahedral charge of vermiculite. In fluorohectorite, which is similar in layer charge and origin of layer charge as the montmorillonite composition studied, the position of the TMA is expected to be similar to the montmorillonite results. These computational models are consistent with single crystal, X-ray diffraction experiments for hydrated TMA-exchanged vermiculite and dried fluorohectorite.

Keywords: interlayer cation and H$_2$O positions, swelling clay minerals, layer charge, phyllosilicates, layer silicates, computational mineralogy
INTRODUCTION

The swelling clay minerals, smectite and vermiculite, are deficient in positive layer charge because of cation substitutions either in the octahedral sheet (e.g., Mg$^{2+}$ for Al$^{3+}$), tetrahedral sheet (e.g., Al$^{3+}$ for Si$^{4+}$) or both sheets (e.g., Brigatti et al., 2011 for a summary). To offset this charge deficiency, the common exchangeable cations in nature (e.g., K, Na, Mg, Fe) may enter the interlayer along with H$_2$O molecules (Bailey, 1980). However, an exchangeable cation may also be an “organic cation” (e.g., any charged hydrocarbon molecule), and these clays generally are less adsorptive of H$_2$O and instead become more organophilic (Johnston, 1996; Cadena and Cazares, 1996 for summaries). Thus, the organoclays not only become important to remove organic contaminants from water, but they are important also in understanding agriculture and soils in general and herbicides specifically (Boyd and Jaynes, 1994). Tetra-alkylammonium (e.g. tetramethylammonium) salts have been used to produce organoclays in the last few decades, acting as surfactants with polar features (ammonium groups) and an apolar moiety (alkyl groups). These apolar groups increase the lipophilic character of the interlayer, and the adsorption capacity of organic molecules increases significantly (Lee et al. 1990). In addition, organic cations (or polar molecules) intercalated in a fixed orientation within the interlayer can also form the basis of nanocomposites. However, little is known about the positions of H$_2$O in the interlayer, and even the position of the hydrocarbon molecule has been called into question. This paper combines structure information from experiment and simulation techniques to determine where H$_2$O molecules reside in the interlayer of swelling clay minerals with
limited hydrophobicity. Furthermore, the simulations explain apparent discrepancies
between some of the experimental data.

Smectite and vermiculite are group names of two different clay mineral groups
closely related in structure (Bailey, 1980). The general formula for smectite,
unconventionally written, is ~[X_{0.3} \cdot nH_2O]^+ [Y_{2-3}Z_4O_{10}(OH)_2]^-, where X is an exchangeable
cation, Y is a small- to medium-sized, octahedrally coordinated cation that is trivalent in
charge if the subscript is 2.0 (= dioctahedral) or divalent if the subscript is 3.0 (=
trioctahedral), Z is a small tetrahedrally-coordinated cation (usually Si$^{4+}$ or Al$^{3+}$), and $n$ may
be variable. The structural formula for vermiculite, in an analogously written formula, is
~[X_{0.5} \cdot nH_2O]^+ [Y_{2-3}Z_4O_{10}(OH)_2]^-, where $n$ is near 4 and the other symbols are the same as
those defined for smectite (Bailey, 1988). Both groups have 2:1 layers (the negative part of
each formula) consisting of an octahedral sheet between two tetrahedral sheets, with the
latter sheets inverted relative to each other. They are mineralogically differentiated by their
2:1 layer charge, with smectites having a layer charge per formula unit of approximately -0.2
to -0.6 (or -0.4 to -1.2 per unit cell) and vermiculites with -0.6 to -0.9 (Bailey 1980). Layer
charge is important because cation-exchange properties, absorption properties, and physical
properties are greatly affected by small changes in layer charge and by the location of the
layer charge (either in tetrahedra or octahedra, or both). Exchange and adsorption
commonly occur between the 2:1 layers, known as the interlayer, or on sites at the broken
edges of the particles, but these latter sites are not considered here. Within each group,
chemical differences separate the different mineral species.
The understanding of the reactivity of organic solutes with such clay minerals requires knowledge of the chemistry and structure of the mineral. Unfortunately, owing to the high degree of 2:1 layer stacking disorder (in smectite and vermiculite) and very small particle size (in smectite), the complete characterization of the crystal structure based on conventional diffraction analysis is extremely difficult, but several approaches have been used to facilitate diffraction studies. The tetramethylammonium (TMA) cation does not produce a high hydrophobicity to the interlayer because the alkyl groups are relatively small. In addition, the TMA cation in the interlayer facilitates the cross linking of adjacent layers to promote stacking order. Combining these materials with TMA intercalation allows sufficiently large crystals to be analyzed by single-crystal X-ray diffraction techniques (Vahedi-Faridi and Guggenheim 1997). Therefore, structural studies have been possible using both experimental and simulation techniques for comparison.

Vahedi-Faridi and Guggenheim (1997) obtained a structure model of TMA-exchanged natural vermiculite from Santa Olalla, Spain (trioctahedral, layer charge primarily originates from tetrahedra, layer charge = -0.85), by single-crystal X-ray diffraction (XRD). They proposed a model (Fig. 1) based on XRD data where the TMA cations are located offset from the center plane of the interlayer by 1.52 Å and one C atom of the TMA tetrahedron is keyed into the silicate tetrahedral-ring cavity. Thus, the TMA cations are arranged with their $C_3$ axis perpendicular to the silicate 2:1 layer, with one face of the NC$_4$ tetrahedron (centered by the N atom and surrounded by the C atoms at the
vertices) parallel to the silicate layers. Each N atom site has an occupancy of 41.8% if all possible positions are occupied, and the TMA cations form two planes within the interlayer where the TMA cations are alternating between these planes. The X-ray study made no assumptions about the interlayer structure, and used difference maps and electron density profiles (Fourier techniques) to derive the structure of the interlayer. Using theoretical studies based on empirical interatomic potentials for vermiculite of similar composition, Čapková et al. (1999) reported that the TMA cations occurred in only the plane at the interlayer center with one of the C-C edges of the NC₄ tetrahedra perpendicular to the layers. This model is clearly contradictory with the electron density profile of the XRD study.

Seidl and Breu (2005) studied a synthetic Li- and F-rich smectite ( trioctahedral, layer charge originates in octahedra, layer charge = -0.5), fluorohectorite, by single-crystal XRD after TMA exchange. In fluorohectorite, TMA cations are essentially in the center plane of the interlayer, in accord with the Čapková et al. (1999) model. Moreover, the C₃ axis of TMA is not perpendicular to the silicate layers, but tilted towards the (001) plane. However, one C-C edge of the NC₄ tetrahedron is perpendicular to the (001) plane. Consequently, the apical methyl group is shifted away from the middle of the tetrahedral-ring cavity to one side (Fig. 1). Because the electron density of the interlayer was highly diffuse (Seidl and Breu 2005), the TMA was treated as a rigid body.

Two other smectites, montmorillonite (dioctahedral, layer charge originates in the Al- and Mg-rich octahedral sheet) and beidellite (dioctahedral, layer charge originates in the
Al-rich tetrahedral sheet), were examined considering the layers and TMA cations as rigid units without optimizations and using empirical interatomic potentials by Čapková et al. (2000), with a layer charge of -0.475 and -0.6, respectively. Two possible TMA models for each smectite were presented. Model 1 has TMA in projection within the silicate tetrahedral rings, but with every alternate 6-ring chain occupied. Model 2 has some TMA projecting on top of silicate tetrahedra and others partially over the silicate tetrahedral rings. Both models indicated that TMA were located on the central plane of the interlayer. Supporting experimental structural data were not presented, and these models are not discussed in detail further.

Vahedi-Faridi and Guggenheim (1997) heat-treated the sample to 250 °C after structural analysis that resulted in a decrease in $d(001)$ value of 0.37 Å, which indicated the presence of H$_2$O in the crystal although there was no apparent XRD scattering from H$_2$O present in the data. Based on these results, they suggested that interlayer H$_2$O is disordered in the structure. In contrast, Seidl and Breu (2005) took great care to dehydrate their crystal before analysis by drying in a high vacuum for 4 days at 90 °C and immersing in perfluorether to prevent rehydration. The theoretical studies by Čapková et al. (1999, 2000) did not consider the possible effects of interlayer H$_2$O.

The fundamental assumption apparently used by Seidl and Breu (2005) in their study was that only one structural model must be correct for TMA-exchanged fluorohectorite vs. vermiculite. In contrast, we assume that both models may possibly be correct and that the
reason for the structural discrepancies requires further clarification. There are many possible parameters to consider that may cause these discrepancies, and they include differences in layer charge, interlayer H\textsubscript{2}O content (including effects of relative humidity), synthetic vs. natural starting material (and possible short-range cation order and layer stacking differences), compositional differences (in the tetrahedra, octahedra, and interlayer), sample preparation differences, and others. The present paper considers interlayer H\textsubscript{2}O content, total layer charge, and location of layer charge, by using quantum mechanical calculations to model the structures of vermiculite and montmorillonite. These models have implications to understand the fluorohectorite results of Seidl and Breu (2005).

**Computational Methods**

*Calculation procedures*

Quantum mechanical calculations of an isolated TMA cation were performed using the Hartree-Fock (HF) approximation including the second-order Moeller-Plesset (MP2) method for describing the electron exchange correlation for all electrons. The molecular electronic structure was calculated with a triple-\(\zeta\) basis set with polarization functions for all atoms including H atoms (MP2/6-311G** level) as implemented in the Gaussian03 program (Frisch et al. 2004). No geometry constraint was applied to the molecule, which was fully optimized using the Berny analytical gradient method. Normal vibration modes were calculated from the force-constant analysis to confirm the nature of the stationary points, which resulted in only positive eigenvalues for the minimum.
Ab initio total energy calculations of the periodic crystal model were performed using density functional theory (DFT) methods based on the numerical atomic orbital (NAO) methodology implemented in the SIESTA program (Soler et al. 2002). The generalized gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof (PBEsol) parameterization of the exchange-correlation function optimized for solids (Perdew et al. 2008). Core electrons were replaced by norm-conserving pseudopotentials (Troullier and Martins 1991). Calculations were restricted to the Γ point in the irreducible wedge of the Brillouin zone. In all structures, the geometry of each atom was relaxed by means of conjugated gradient optimizations at constant experimental volume. In SIESTA, the basis sets are made of strictly localized numerical atomic orbitals (NAOs) with a localization cut-off radius corresponding to an energy shift of 270 meV. The basis sets used here are double-Z polarized (DZP) following the perturbative polarization scheme. This approach was successfully used in previous calculations on phyllosilicates (Hernández-Laguna et al. 2006).

A uniform mesh with appropriate plane-wave cut-off energy is used to represent the electron density, the local part of the pseudopotential, and the Hartree and exchange-correlation potentials. Total energy calculations were performed with cut-off energy values of 150 Ry. These conditions are consistent with previous studies with phyllosilicates (Sainz-Díaz et al. 2005).

Model development
Model development involved defining each component of the phyllosilicate and then assembling these components. Analyses were made using increasingly complex assemblages.

**The basic 2:1 layer.** A periodic model of the crystal structure of vermiculite was generated from the experimental atomic coordinates and cell parameters given in Vahedi-Faridi and Guggenheim (1997). To create a supercell of a reasonable size for modeling, the structural formula of the vermiculite 2:1 layer used in the modeling experiments was simplified to the form: \((\text{Mg}_{5.25}\text{Al}_{0.75})(\text{Si}_{5.5}\text{Al}_{2.5})\text{O}_{20}(\text{OH})_4\) per unit cell, where the layer charge per unit cell is -1.75 (LC models). Additional models with very low charge (-1.25) \((\text{Mg}_5\text{Al})(\text{Si}_{5.75}\text{Al}_{2.25})\text{O}_{20}(\text{OH})_4\) (VLC models) and high charge (-2) \((\text{Mg}_{5.5}\text{Al}_{0.5})(\text{Si}_{5.5}\text{Al}_{2.5})\text{O}_{20}(\text{OH})_4\) (HC models) were generated by adjusting the chemical composition of the layer (Table 1). Maximum separations between cation substitutions in the tetrahedral and octahedral sheets are used because these configurations are more stable based on previous calculations (Palin et al. 2004; Sainz-Díaz et al. 2003). Each model consisted of a supercell of 2 x 2 x 1 vermiculite subcells (Fig. 2). To compensate the layer charge in this supercell, TMA cations, previously optimized by quantum mechanical calculations, were placed in the supercell to explore the different possible arrangements in the interlayer.

**Models involving intercalated TMA.** The TMA cation was obtained from atomic coordinates extracted from XRD data (Vahedi-Faridi and Guggenheim 1997) and initially optimized at MP2/6-311G** level and later reoptimized using the DFT-SIESTA approach before intercalation. Within the 2 x 2 x 1 supercell, HC models (Fig. 2) were further defined...
as an HC1 model consisting of eight TMA cations located with each having one methyl
group in the center of the tetrahedral-ring cavities, placing alternating four TMA cations
near the lower silicate layer and four TMA cations near the upper silicate layer. For each
model, TMA positions were adjusted depending on the location of the local charge in the
layer. The HC2 model is similar to the HC1 model, but four TMA cations are arranged
such that two TMA pairs are located in the same ab site, where the centroids of the cations
have the same x and y values but with different z coordinate values forming two-TMA
pillars; in HC3, all TMA cations form pairs in the same ab site with different z coordinate
values, but in the four central cavities of the supercell. The HC4 model is similar to HC2 but
three TMA cations are located to form two-TMA pillars. In each LC model, there are seven
TMA cations per supercell of vermiculite; three TMA cations are located within the upper-
layer tetrahedral-ring cavity and four cations in the lower-layer, alternately located in the
tetrahedral-ring cavities with greatest local charge, and one pair of cavities is without TMA.
In the VLC models, the five TMA cations are located as in HC1 (VLC1) or forming pairs
alternately as in HC2 (VLC2).

Models involving H2O + TMA. Different numbers of H2O molecules were added to
TMA-vermiculite models in a disordered fashion. In each case, there are seven TMA cations
and eight pairs of tetrahedral-ring cavities per 2x2x1 supercell (simulation cell). The cavity
pair without TMA is filled with more H2O molecules than the cavity pair with each TMA.
For example, the LC-W1 model has 9 water molecules per simulation cell: one H2O
molecule is located in each cavity at the opposite site to each TMA and two water molecules
are located in the cavity without TMA (4.4 % w/w of total water content); LC-W2 has 18
water molecules per simulation cell: same as LC-W1, but adding two H$_2$O molecules per
TMA and four water molecules in the cavity without TMA (9.2 % total water content); LC-
W3 has 27 water molecules per simulation cell: adds three H$_2$O molecules per TMA and six
water molecules in the cavity without TMA (12.0 % total water content); LC-W4 has 34
water molecules per simulation cell: adds four H$_2$O molecules in each tetrahedral-ring cavity
opposite from each TMA site and six water molecules in the cavity without TMA (14.5 % of
water) (Table 1). All water molecules were placed randomly to avoid electrostatic
repulsions.

In addition, a montmorillonite model with TMA was also studied as a model with
octahedral charge, but without tetrahedral charge, [TMA \cdot 8H$_2$O]$^+$ [(Al$_3$Mg)(Si$_8$)O$_{20}$(OH)$_4$]$^-$, with 8 water molecules per unit cell. In this model with low interlayer charge, only one
cavity is occupied by TMA and 4 water molecules are located between the TMA and the
other adjacent tetrahedral sheet. The tetrahedral-ring cavity without TMA is filled with 4
water molecules.

RESULTS

*TMA molecule.* The molecular structure of TMA as a gas was analyzed after
optimizing at MP2/6-311G**, and DFT levels. The latter also included optimizing the TMA
molecule in an isolated periodic box. Each method reproduced the experimental values
(Vahedi-Faridi and Guggenheim 1997) of H-C-N and C-N-C angles (109°-109.5°), and C-N
(1.47-1.50 Å) and C-H (1.09-1.12 Å) bond lengths.
TMA-intercalated vermiculite structures. In the optimization calculations of the HC1 model, all TMA cations are displaced to the center plane of the interlayer region with the C₃ axis no longer perpendicular to the silicate layers but tilted towards the \(ab\)-plane as in the model of Seidl and Breu (Fig. 3a). In the HC2 and HC4 models, initially one TMA molecule is located near the upper tetrahedral-ring cavity and alternately one TMA molecule is located near the lower ring cavity as in HC1; however, in these models this arrangement produces some TMA cations that form two-TMA pillars. In the optimized structures these latter TMA cations are located in two levels of the interlayer as two-TMA pillars (Fig 3b) and the remaining TMA cations are displaced to the center plane of the interlayer region with the C₃ axis no longer perpendicular to the silicate layers but tilted towards the \(ab\)-plane as in the model of Seidl and Breu. In calculations involving HC3, all TMA cations are located forming pillars (4 keyed in the upper layer and 4 keyed in the lower layer). Geometry optimizations maintain all TMA cations oriented in two planes in the interlayer maintaining the pillars (Fig. 3c). The HC1 structure is the most stable of these models and the two-TMA pillars produce a high instability to the complex (Table 1). The same behavior was observed in the VLC models with lower interlayer charge, where VLC1 is more stable than VLC2 (Table 1).

Intercalations of TMA + \(H_2O\) in vermiculite. In all optimized models with water, the water molecules appear disordered. Geometry optimizations in LC-W1 and LC-W2 models yielded shifts of TMA cations, where TMA cations are rotated and located in the central plane of the interlayer, similar to the dry TMA-exchanged vermiculite structure. The water molecules form H bonding to each other and to the basal tetrahedral O atoms. For LC-W1,
water molecules are in the tetrahedral cavities and do not interact with TMA cations. The H-O-H plane is parallel to the (001) plane and H bonds form between the water-molecule H atoms and the O atoms of the basal tetrahedral plane and between the water-molecule O atoms and the H atom of the OH group in the octahedral sheet. The orientation of the O-H vector in the octahedral sheet has an inclination angle of 90º with respect to the (001) plane. In the LC-W3 model, geometry optimization produced a pattern where TMA cations alternate in two planes in the interlayer. However, these TMA cations are not located with the C atom in the tetrahedral-ring cavity and most are rotated. The water molecules are connected forming a H bonding network between TMA and the basal tetrahedral O atoms. Finally, optimization of the LC-W4 model resulted in two planes of TMA cations with the C atom keyed to the tetrahedral-ring cavity to reproduce the model of Vahedi-Faridi and Guggenheim (Fig. 4a). The H atoms of the methyl groups of TMA, which are close to the tetrahedral-ring cavity, form H bonds with the basal oxygen atoms with distances of 1.77 – 1.93 Å. Water molecules form a H bonding network with other water molecules and also strong H bonds with basal tetrahedral oxygen atoms (1.65-1.43 Å) as well as with the octahedral OH groups (1.38 Å between the O atom of H₂O and the H atom of the OH group within the octahedral sheet).

**Intercalations of TMA + H₂O in montmorillonite.** The main difference between vermiculite and hectorite is the lower tetrahedral charge in hectorite than in vermiculite. Hence, a model of montmorillonite without tetrahedral charge was chosen, to explore the effect of the tetrahedral charge in the disposition of TMA in the interlayer. The optimization of both models, with 8 water molecules per unit cell, yielded the TMA molecule displaced
from the interlayer center. The TMA molecule is close to one tetrahedral-ring cavity and some water molecules are between the TMA and the opposing side of the interlayer. This disposition is similar to that observed in vermiculite. However, in montmorillonite the methyl group is oriented to the tetrahedral-ring cavity such that it is less anchored to this cavity than in vermiculite (Fig. 4b). For example, the H atoms of the methyl groups of TMA, which are close to the tetrahedral-ring cavity, form weaker interactions with the basal tetrahedral O atoms (1.99 – 2.26 Å) than in vermiculite. Water molecules are disordered and no water molecule was found trapped in the tetrahedral cavities.

Discussion

The effect of $H_2O$ in TMA-exchanged vermiculite. The number of disordered water molecules has a critical role in the crystal structure of this organo-exchanged clay mineral. Where there are a sufficient number of water molecules, TMA cations are located alternating in two planes, which is consistent with the Vahedi-Faridi and Guggenheim model. However, in the absence of water molecules, TMA cations are distributed in one plane at the center of the interlayer (Fig 5a), as found by Seidl and Breu (2005) in hectorite and modeled in vermiculite and montmorillonite by Čapková et al. (1999, 2000). Because of the high hygroscopicity of TMA, the presence of water molecules in the interlayer is probably the case for most samples, unless special effort is made to dehydrate the material.

With the presence of only one water molecule per TMA cation, an asymmetry in the density profile of N atoms along the [001] direction is observed (Fig. 5b). However, the
TMA cations are mainly in the interlayer center because the water molecules are trapped in the tetrahedral cavity with high tetrahedral charge and they do not interact with the TMA cations. In the LC-W4 structure the TMA cations are surrounded by water molecules forming a cage. This cage is similar to a clathrate hydrate where the basal oxygen atoms of the closest tetrahedral-ring cavity act as coordinated water molecules completing the hydration cage. Similar cages are observed experimentally in hydrates of TMA hydroxide (Ratcliffe et al. 1990). In our case, the anion is the negative charge provided by the 2:1 layer, and the basal oxygen atoms of the 2:1 layer form a hexagonal face of the hydrate cage. Nevertheless, a hydrophobic zone occurs between the methyl groups with no water molecules associated with the TMA cations.

The shift of the N atom (as a center of the TMA molecule) with respect to the interlayer center (1.22 Å, Fig. 5a) indicates that the TMA position is not only related to the tetrahedral charge but also to the H bonds between the methyl H atoms and the basal oxygen atoms of the tetrahedra.

Where water molecules are randomly distributed in the interlayer, however, there is local ordering as observed in the density profile of the O atoms of water molecules along the [001] direction in the interlayer space. Two peaks are observed for the O atoms in a similar way as to the N atoms of the TMA cations. This indicates that the water molecules occupy the space vacated by the TMA shift from the interlayer center. Nevertheless, these peaks are wider and with lower relative intensity with respect to the vermiculite peaks density than those of the N atoms of TMA cations owing to the high disorder of the water molecules. Two additional peaks are observed at the same level of the basal oxygen atoms of the
tetrahedra indicating the strong interaction of one water molecule with the O atoms of the cavity formed within the tetrahedral ring and the octahedral hydroxyl group (Fig. 6). Considering the radial distribution function of the water molecule atoms in the interlayer with TMA cations, the O…O, H…H and O…H distances are slightly shorter than in other hydrates (Martos-Villa et al. 2013) probably owing to the confined space of the vermiculite interlayer (Fig. 6).

**Effect of H₂O in TMA-exchanged montmorillonite.** The asymmetry of the TMA cations with respect to the interlayer center observed in vermiculite is apparently attributed to the relatively high charge of vermiculite originating from substitutions in tetrahedral sites. However, this asymmetry is also observed to a lesser degree in the montmorillonite model with no tetrahedral charge. This asymmetry is smaller than in vermiculite, owing to the weaker interactions between the methyl H atoms of TMA and the basal oxygen atoms of the tetrahedra. Consequently, the C-N bond of the methyl group oriented towards the tetrahedral-ring cavity does not have the perpendicular orientation with respect to the tetrahedral sheet, unlike the arrangement that occurs in vermiculite. The shift of the N atom of TMA with respect to the center of the interlayer is 0.87 Å (Fig. 5c), which is smaller than that observed in vermiculite (1.22 Å) (Fig. 5a). In this case, the water molecules do not interact with the tetrahedral cavities so strongly as in the vermiculite samples due to the lack of the tetrahedral charge and the inclination of the octahedral OH group which is not oriented towards the interlayer.
Quantum mechanical calculations are capable of clarifying why differences occur between the hydrous and anhydrous TMA models of vermiculite, montmorillonite and fluorohectorite. However, such an analysis requires that all reasonable models need to be anticipated when developing a theoretical study, and thus it is especially useful to combine both theoretical and experimental approaches.

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References


Captions of Figures

Figure 1. Arrangement of TMA molecules in the interlayer of vermiculite. Left: Vahedi-Faridi and Guggenheim model; Right: Seidl and Breu model. N, C, and H atoms of TMA are represented in green, grey and white balls respectively. O, Si, and Al atoms from vermiculite tetrahedral sheet are represented in red, yellow and purple respectively.

Figure 2. Cation arrangements of the (a) octahedral sheet, (b) upper tetrahedral sheet of 2:1 layer, (c) lower tetrahedral sheet of 2:1 layer (the TMA, which are close to the tetrahedral-ring cavities of the upper and lower tetrahedral sheets, are represented as blue triangles), and (d) lateral view of parts of the 2:1 layer and interlayer of vermiculite. The Mg, Al, Si, O, C, N and H atoms are in green, pink, yellow, red, black, blue, and light grey, respectively. Parts (b), (c) and (d) show the projections of the TMA cations for the initial HC1 model. (all TMA are dispersed, TMA cations which are in the front are highlighted as spheres). Parts (e) and (f) show the initial HC2 and HC3 models, respectively.

Figure 3. TMA orientations in the interlayer of the optimized vermiculite model HC1 (a), HC2 (b), and HC3 (c). The Mg, Al, Si, O, C, N and H atoms are in green, pink, yellow, red, black, blue, and light grey, respectively. The TMA cations are highlighted as balls.

Figure 4. Optimized vermiculite models with vermiculite + TMA + H₂O, LC-W4 (a) and montmorillonite + TMA + H₂O (b). The Mg, Al, Si, O, C, N and H atoms are in green, pink, yellow, red, black, blue, and light grey, respectively. TMA cations which are in the front are highlighted as spheres.

Figure 5. Density profiles, along the c axis of the interlayer, of the atoms in vermiculite-TMA models HC1 (bottom profile in a), LC-W4 (top profile in a) and LC-W1 (b); and the hydrated TMA-montmorillonite (c). Dashed black lines represent N atoms density; Black lines represent vermiculite atoms density; Grey dotted lines represent the interlayer cations N atoms density in the experimental crystal structure (Vahedi-Faridi and Guggenheim, 1997).

Figure 6. Density profile of the O atoms (in dashed line) of water molecules in the LC-W4 model (a) (solid line represents the profile of the tetrahedral and octahedral layers of vermiculite), and radial distribution functions of O…O (b), H…H (c), and O…H (d) distances of the water molecules in the interlayer of LC-W4 model.
Fig 1.
Fig. 2

HC1 (d)
Fig 2 (cont.)

HC2 (e)

HC3 (f)
Fig. 4
Fig. 5.-
a) Relative concentration vs. C(001) Distance (Å) for Water O atoms and Vermiculite atoms.

b) Plot of r_{oo} / Å vs. r_{oo} for O-O interactions.
Fig. 6.-
Table 1.- Models of TMA-vermiculite complex and relative energy (in eV) within each group of samples.

<table>
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<tr>
<th>sample</th>
<th>Unit cell formula</th>
<th>ΔE (eV)</th>
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<tbody>
<tr>
<td>VLC1</td>
<td>TMA$<em>{1.25}$ (Mg$</em>{5.5}$Al$<em>{0.5}$)Si$</em>{5.5}$O$_{20}$OH$_4$</td>
<td>0.0</td>
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<td>VLC2</td>
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<tr>
<td>HC1</td>
<td>TMA$<em>2$ (Mg$</em>{5.5}$Al$<em>{0.5}$)Si$</em>{5.5}$O$_{20}$OH$_4$</td>
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<td>HC2</td>
<td>TMA$<em>2$ (Mg$</em>{5.5}$Al$<em>{0.5}$)Si$</em>{5.5}$O$_{20}$OH$_4$</td>
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<td>HC3</td>
<td>TMA$<em>2$ (Mg$</em>{5.5}$Al$<em>{0.5}$)Si$</em>{5.5}$O$_{20}$OH$_4$</td>
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<td>HC4</td>
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<td>LC-W1</td>
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<td>LC-W2</td>
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<td>LC-W3</td>
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<td>LC-W4</td>
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