

Molecular Simulations of the Tetramethylammonium Vermiculite Crystal Structure

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INTRODUCTION

Vermiculite is a trioctahedral 2:1 phyllosilicate with a structural composition of $IC_{x,y}(Si_{8-x}Al_x)(Mg_{6-y}Al_y)O_{20}(OH)_4$. It has a high cation exchange capacity and extraordinary absorption properties. However, in aqueous media the adsorption in the interlayer space of organic molecules is limited. Tetraalkylammonium salts have been used to produce organoclays traditionally in the last decades, acting as surfactants with a polar moiety (ammonium group) and an apolar zone (alkyl groups). These apolar groups increase the lipophylia of the interlayer space and the adsorption capacity of organic molecules increases significantly.

The tetramethylammonium (TMA) cation does not provide a high hydrophobicity to the interlayer space because the alkyl groups are very small, however its structure facilitates the ordering of mineral layers being possible the generation of crystal structures of vermiculite-TMA complexes with a high ordering degree.

Vahedi-Faridi and Guggenheim (1997) obtained a high quality crystal structure of TMA-vermiculite. In order to interpret the x-ray-diffraction (XRD) studies, they proposed a model where the TMA molecules are located offset from the center of the interlayer region by 1.52 Å, one C atom of the TMA tetrahedron is keyed into the silicate ring of the tetrahedral cavity, so the TMA molecules are arranged with their C_3 axis perpendicular to the silicate layer, bringing one face of the NC_4 tetrahedron parallel to the silicate layers. These TMA molecules should be alternating forming two layers in the interlayer space in order to justify the $d(001)$ spacing (Fig. 1).

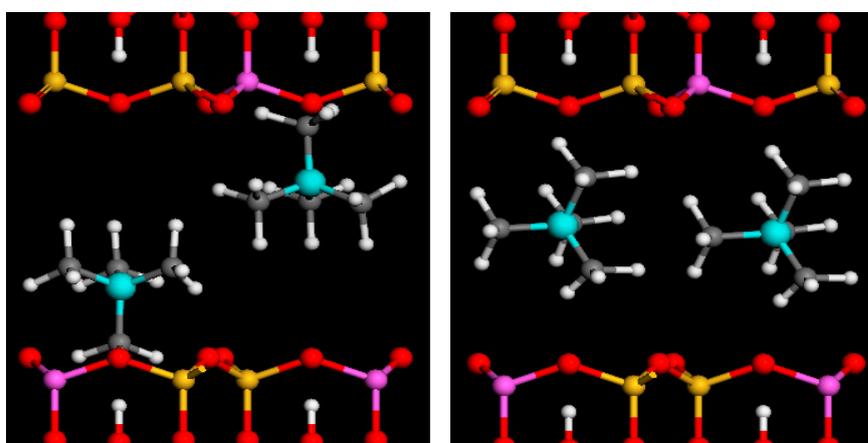


Fig. 1. Arrangement of TMA molecules in the interlayer space of vermiculite. Left: Vahedi-Faridi and Guggenheim model; Right: Seidl and Breu model. N, C, and H atoms of TMA are represented in blue, grey and white balls respectively. O, Si, and Al atoms from vermiculite tetrahedral sheet are represented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

However, later crystallographic studies of TMA-hectorite crystals showed different positions for the TMA adsorption sites (Seidl and Breu, 2005). The organic interlayer cations are shifted by 1.26 Å from the middle of the interlayer space, considerably less than the 1.52 Å reported by Vahedi-Faridi and Guggenheim (1997). Moreover, the C_3 axis of TMA is no longer perpendicular to the silicate layers but tilted towards the ab -plane. Consequently, the apical methyl group is shifted away from the middle of the hexagonal tetrahedral cavity (Fig. 1).

On the other hand, theoretical studies of TMA-vermiculite based on empirical interatomic potentials supported the model of Seidl and Breu (2005) with the TMA molecules arranged in one layer in the center of the interlayer space (Capkova et al., 1999), with one of the C-C edge of the NC_4 tetrahedra perpendicular to the silicate layers. However, this model cannot explain the XRD diffractogram of the TMA-vermiculite crystal. This discrepancy remains still open. One of our aims is to

find a model that helps to understand the experimental behavior and to clarify these discrepancies.

COMPUTATIONAL METHODOLOGY

Quantum chemical calculations of TMA molecules were performed using GAUSSIAN03 at MP2/6-311** level. Ab initio total energy calculations of the periodic crystal models were performed using DFT methods at GGA/PBEsol/DZP level with SIESTA. Total energy calculations were performed with cut-off energy values of 150 Ry. These conditions are consistent with our previous work (Sainz-Díaz et al., 2005). Density profiles are calculated to analyze the TMA distribution in the interlayer space.

MODELS

A periodic model of the crystal structure of vermiculite was generated based on experimental atomic coordinates and lattice cell parameters (Vahedi-Faridi and Guggenheim, 1997). In order to create a supercell of a reasonable size

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for modeling, the structural formula of Santa Olalla vermiculite used in the experiments, was simplified to the form: $(\text{Si}_{5.5}\text{Al}_{2.5})(\text{Mg}_{5.25}\text{Al}_{0.75})\text{O}_{20}(\text{OH})_4$ per unit cell, where the layer charge is (-1.75). An additional model with higher charge was generated, $(\text{Si}_{5.5}\text{Al}_{2.5})(\text{Mg}_{5.5}\text{Al}_{0.5})\text{O}_{20}(\text{OH})_4$. Maximal dispersion was used for the cation substitutions in the tetrahedral and octahedral sheets. A supercell $2 \times 2 \times 1$ was created. To compensate the layer charge of (-7 or -8) in this supercell, seven (or eight) TMA cations previously optimized by quantum chemical methods were placed into the supercell and arranged according to model suggested by Vahedi-Faridi and Guggenheim. Initial lattice parameters of $2 \times 2 \times 1$ supercell are: $a = 10.7 \text{ \AA}$, $b = 18.5 \text{ \AA}$, $c = 13.6 \text{ \AA}$ and $\alpha = \gamma = 90^\circ$, $\beta = 97.8^\circ$.

Different models of TMA-vermiculite $2 \times 2 \times 1$ were made varying the layer charge, and TMA initial placement within the interlayer. Model with high charge: **HC1**: for all (8) pairs of cavities per supercell, 8 TMA molecules are located with methyl groups in the center of silicate ditrigonal cavities, placing 4 TMA near the lower silicate layer and 4 TMA near the upper silicate layer alternating; Low charge model: **LC1**: with 7 TMA molecules per supercell, placing 3 TMA in the upper layer and 4 TMA in the lower layer alternating choosing the silicate ditrigonal cavities with more local charge, and one pair of cavities is without TMA.

RESULTS AND DISCUSSION

Vermiculite-TMA Crystal Structure.

All vermiculite-TMA dry models have shown that after constant volume geometry optimization, TMA molecules are located in the centre of the interlayer region, with the C_3 axis of TMA no longer perpendicular to the silicate layers but tilted towards the ab -plane (Fig. 2) as in the Seidl and Breu (2005) model.

Vermiculite-TMA-Water Crystal Structure

In order to understand and clarify the reported discrepancies by other authors and our above results with dry models, our initial hypothesis is that some additional atoms not detected experimentally should exist between TMA molecules and the basal tetrahedral oxygens in order to maintain the disposition of TMA alternating in two layers. These additional atoms must not

provide extra charge, should be electronically lights, and should be highly disordered in such a way that they cannot be detected by XRD. Water molecules were the best option.

Different numbers of water molecules for each TMA-vermiculite model were added to vermiculite-TMA structure, like the LC1 model, forming pre-oriented hydrogen bonded network in order to facilitate calculations to converge: **W1** model: with one water molecule added in each cavity at the opposite site to each TMA; **W2**: the same but adding 4 water molecules in each ditrigonal cavity at the opposite site to each TMA; and **W3**: adding 3 molecules in each ditrigonal cavity at the opposite site to each TMA. In all cases there are 7 TMA and 8 pairs of cavities and the cavity pair without TMA will be filled with water molecules.

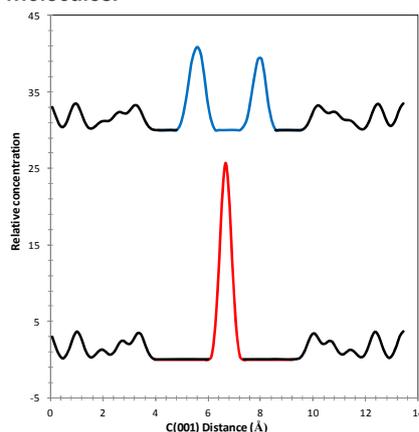


fig 2. Density profiles along the c axis of the interlayer space of vermiculite-TMA **W2** (top profile) and **HC1** (bottom) models. Black lines represent vermiculite crystal structure; red and blue lines represent N density in **HC1** and **W2** models, respectively.

Geometry optimizations in **W1** model yielded a shift of organic molecules, where TMAs are rotated and located in the centre of the interlayer, like in vermiculite-TMA dry structures as in the Seidl and Breu (2005) model. In **W3** model, geometry optimization yielded the TMA molecules alternating in two layers of, but those TMAs are not located with the C arranged to the silicate ring, and most of them are rotated. Finally, optimizations of **W2** model resulted in two layers of TMA molecules with the C atom keyed to the silicate rings (Fig. 2) reproducing the model of Vahedi-Faridi and Guggenheim.

Variable volume calculations of those three models rise c axis values closer to experimental, although for **W3** and **W2**

models c axis gets close to 16 \AA . This can be justified because of the swelling caused by such quantity of water molecules.

CONCLUSIONS

Quantum mechanical calculations have been able to clarify the discrepancy about the crystal structure of TMA-vermiculite and the distribution of TMA molecules in vermiculite interlayer.

We find that a certain amount of disordered water molecules has a critical role in the crystal structure of this organoclay. When there is enough amount of water molecules, TMA molecules are located alternating in two layers like Vahedi-Faridi and Guggenheim model, but in absence of water molecules, TMA are distributed in one layer at the center of the interlayer space like the Seidl and Breu model. Taking into account the high hygroscopicity of TMA, the presence of water molecules in the interlayer space is highly expected justifying the crystal structure reported by Vahedi-Faridi and Guggenheim.

This work is a clear example of cooperation between theoretical and experimental research.

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