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

Ruben Martos-Villa,[1] Stephen Guggenheim,[2] and C. Ignacio Sainz-Díaz[3,*]

[1]Facultad de Ciencias del Mar y Ambientales, Universidad de Cádiz, Av. República Saharaui s/n, 11510 Puerto Real, Spain
[2]Department of Earth and Environmental Sciences, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607, U.S.A.
[3]Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada, Av. de las Palmeras, 4, 18100-Armilla, Granada, Spain

Abstract

Organoclays, unlike natural clays with inorganic cations that often have a hydration shell of H_2O molecules, are organophylic and less adsorptive of H_2O. 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 H_2O in the interlayer when these molecules intercalate along with medium-sized hydrocarbon molecules, such as tetramethylammomium (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_2O in the interlayer of vermiculite and montmorillonite were investigated by using atomistic computational methods. Interlayer H_2O content, layer charge, and location of layer charge were considered. For both vermiculite and montmorillonite and where the number of H_2O 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_2O molecules are disordered. In the absence of H_2O, 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_2O positions, swelling clay minerals, layer charge, phyllosilicates, layer silicates, computational mineralogy