DENSITY FUNCTIONAL THEORY (DFT) STUDY OF THE HYDRATION STEPS OF 
Na⁺/Mg²⁺/Ca²⁺/Sr²⁺/Ba²⁺-EXCHANGED MONTMORILLONITES

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Abstract—Theoretical models of the mechanical properties of hydrated smectites, saturated with a variety of cations, are of much value in determining the potential for their use in various applications, including clay-polymer nanocomposites, but the development of such models is still in its infancy. The purpose of this study was to calculate the effects of divalent cations on the structural and mechanical elasticity of montmorillonite under different degrees of hydration. A theoretical study of the swelling and hydration behavior of montmorillonite was, therefore, undertaken using density functional theory (DFT) to investigate the basal spacing behavior of the homoionic montmorillonite with varying amounts of water in the interlayer space. The effect of the degree of the hydration of divalent interlayer cations (Mg²⁺/Ca²⁺/Sr²⁺/Ba²⁺) on the structure expansion of the interlayer space was analyzed. In addition, the results obtained were compared to calculations performed on the montmorillonite model with a monovalent cation (Na⁺). The basal spacing (d₀₀₁) is governed by the size and the degree of hydration of the counterions. The structures containing divalent cations are more compact than structures with monovalent cations. Back-exchanged montmorillonite was found to have the largest d₀₀₁ value for any degree of hydration (‘dry’, one water layer, or two layers). The basal spacings of ‘dry’ montmorillonite exchanged with small cations, Mg²⁺ and Ca²⁺, are very similar. In hydrated models, the d₀₀₁ expansion correlates with the ionic radius of the interlayer cation. The dependence of the total electronic energy on the volume expansion was calculated. From the energetic curves, bulk modulus (B₀) was obtained by fitting in order to show how the compliance of the material depends on the type of interlayer cation and on the degree of hydration. With increasing water content in the interlayer space, the bulk modulus decreased, suggesting that the c-axis compression becomes easier with increasing hydration of the clay mineral. The values of the bulk modulus in hydrated systems are less sensitive to the type of the interlayer cation.

Key Words—Hydration, Density Functional Theory, Interlayer Cation, Montmorillonite.

INTRODUCTION

Clay minerals are aluminosilicates which predominate in mineral fractions of soils and sedimentary rocks (Perkins, 1998; Velde, 1995). They are also important for industrial and technological applications due to their chemical and catalytic activities, e.g. as sorbents, filters, or waste deposits (Giese and van Oss, 2002; Bailey, 1988). Generally, these minerals consist of one or two layers of polymerized silicon-oxygen tetrahedra and one layer of polymerized aluminum or magnesium oxygen/hydroxyl octahedra stacked on top of each other in a well-defined manner (Velde, 1995). Montmorillonite belongs to the smectite family of 2:1 clay minerals; it possesses a negative layer charge, q, due to isomorphic substitutions mainly in the octahedral sheet (Mg²⁺ for Al³⁺). Typical values of q for smectites are in the range 0.2–0.6 [e]. The excess negative charge is normally compensated by interlayer counterions. The cations and the charged clay mineral surface can interact strongly with polar solvents and easily undergo hydration. Smectites can exchange interlayer cations (usually in hydrated form) and also have a tendency to swell by the incorporation of large amounts of water molecules. These minerals also intercalate various organic molecules into the interlayer space.

The hydration and dehydration reactions of montmorillonite are important in many geological processes and have been linked to phenomena as diverse as sediment overpressurization and petroleum migration. Characterized by significant swelling capacities, montmorillonites are used widely for the intercalation of various species, from small molecules to polymers, into the interlayer space (Kato and Usuki, 2000). The design of new clay-polymer nanocomposites with improved mechanical (Liu et al., 2003; Wan et al., 2003; Zhang et al., 2005), heat resistant (Qin et al., 2003), or coating (Majumdar et al., 2003) properties is a field of intense research. Clays are also used as molecular-sieve catalysts (Kantam et al., 1998), ion exchangers, and adsorbents (Manju et al., 1999).

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