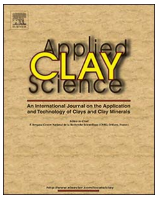
Applied Clay Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay



Research paper

Effects of charge density on the hydration of siloxane surface of montmorillonite: A molecular dynamics simulation study

Wei Shen[a], Lin Li[a,b], Huijun Zhou[a,b], Qing Zhou[b], Meng Chen[b], Jianxi Zhu[b,*]

[a] *University of Chinese Academy of Sciences, Beijing 100049, China*
[b] *Guangdong Provincial Key Laboratory of Mineral Physics and Materials, CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, CAS, 510640, China*

ARTICLE INFO

Keywords:
Montmorillonite
Charge density
Hydration
Molecular dynamics simulation

ABSTRACT

The physicochemical properties of clay minerals strongly depend on their hydration characteristics which therefore have drawn great concerns from different research communities. In the present work, the effects of charge density of montmorillonite (Mt) on the hydration characteristics of its interlayer spaces, particularly the siloxane surface, were studied using classical molecular dynamics (MD) simulations. Four Mt. models with various octahedral charges are established, and these charges are compensated with tetramethylammonium cation (TMA). The simulation results showed that water molecules within the hydration layer of siloxane surface will donate hydrogen atoms to form H-bond with the surface oxygen atoms, while those surrounding TMA only slightly have their oxygen atoms point towards TMA. In addition, water molecules prefer to first hydrate the siloxane surface and then the TMA as the water content increases. These findings indicate that water molecules have stronger hydration interaction with siloxane surface than with TMA, and TMA can be ideal counterbalance cation in terms of studying the hydration characteristics of siloxane surface. Charge density can significantly influence the hydration of TMA-Mt. Although increasing charge density will not lead to the formation of stronger H-bond (i.e., no obvious reduction of H-bond length) between water molecules and siloxane surface, water molecules are more likely to be drawn to the siloxane surface and form more H-bonds between them. Subsequently, the hydration energy increases and the mobility of water molecules decreases as the charge density rises. These findings show that charge density can evidently influence the hydrophobicity of siloxane surface, which may further influence its interaction with organic species, e.g., the adsorption of organic contaminants.

1. Introduction

Swelling clay minerals such as smectite possess two-dimensional nanosized layering structure and have found wide applications in a variety of areas, e.g., engineering, petrological processes, and nanomaterial synthesis (Bergaya et al., 2006; Chen et al., 2008; Anderson et al., 2010). In addition, due to their ubiquitous presence in the nature and strong binding capacity toward various contaminants, they have drawn much environmental concerns as well (Bergaya et al., 2006; Lee and Tiwari, 2012; Sarkar et al., 2012; Dong, 2012). Numerous studies have shown that the applicability of clay minerals in many fields directly relies on their interlayer hydration (Bergaya et al., 2006; Sarkar et al., 2012; Dong, 2012; Zhu et al., 2009). For example, interlayer hydration of clay minerals is of critical importance for their formation of drilling mud (Bergaya et al., 2006; Chen et al., 2008; Anderson et al., 2010; Lee and Tiwari, 2012; Sarkar et al., 2012; Dong, 2012); the interactions of clay minerals with various guest molecular species, such as modifiers (for synthesizing functional materials), contaminants (for environmental remediation), and medicines/pesticides (for controlled release formula), can be significantly affected by interlayer hydration as well (Bergaya et al., 2006; Maitland, 2000). In this regards, the hydration characteristics of clay minerals have received great interests from various research communities (Marry et al., 2008; Liu and Lu, 2006; Mignon et al., 2010).

Up to now, a number of experimental techniques and molecular modeling methods have been applied to study the hydration characteristics of interlayer spaces of clay minerals (Madejova et al., 2002; Tambach et al., 2004a,b; Malikova et al., 2007; Tenorio et al., 2008; Marry et al., 2011; Morodome and Kawamura, 2011; Shapley et al., 2013), and the effects of various factors, such as water content, counterbalance cations, and the type of clay minerals, on the hydration have been well examined. Based on previous studies, it is generally recognized that interlayer cations

---

[*] Corresponding author.
E-mail address: zhujx@gig.ac.cn (J. Zhu).

http://dx.doi.org/10.1016/j.clay.2017.09.005
Received 12 June 2017; Received in revised form 30 August 2017; Accepted 4 September 2017

Please cite this article as: Shen, W., Applied Clay Science (2017), http://dx.doi.org/10.1016/j.clay.2017.09.005

with strong hydration capacity (e.g., Na^+, Li^+) tend to form outer-sphere surface complexes on the siloxane surface, and can cause extensive interlayer swelling and hydrophilic interlayer environment (Bergaya et al., 2006; Mignon et al., 2010; Sposito et al., 1999). On the contrary, cations with weak hydration capacity (e.g., K^+, Cs^+) form inner-sphere complexes, and clay minerals then have less swelling capacity and less hydrophilic interlayer environment (Bergaya et al., 2006; Liu and Lu, 2006; Mignon et al., 2010; Sposito et al., 1999; Yariv and Cross, 2001; Qu et al., 2011). Tetrahedral substitution within the layers of clay minerals causes high local charge density on the siloxane surface, leading to hydrophilic siloxane surfaces with a relatively strong interaction with water molecules (Bergaya et al., 2006; Mignon et al., 2010; Sposito et al., 1999); while octahedral substitution has mild effects on the local charge density on the siloxane surface, which then leads to less hydrophilic siloxane surfaces with relatively weak interaction with water molecules (Bergaya et al., 2006; Mignon et al., 2010; Sposito et al., 1999).

The findings about the hydration characteristics of clay minerals are of high importance for the effective applications of clay minerals. For example, organic cations with weak hydration capacity have been used to create hydrophobic interlayer spaces for clay minerals. The resulting materials, also known as organoclays, can effectively uptake hydrophobic organic contaminants (HOCs) and have found applications in environmental remediation (Bergaya et al., 2006; Yariv and Cross, 2001; Zhu et al., 2012a,b; Chen et al., 2005). Moreover, clay minerals with octahedral substitutions have been considered to be more suitable for synthesizing organoclays, as their siloxane surfaces are more hydrophobic (Bergaya et al., 2006).

Besides the difference of charge types (i.e., octahedral charge vs. tetrahedral charge), clay minerals from different sources generally contain different charge densities, which can significantly affect the physicochemical properties of clay minerals and their derivatives as well (Zhu et al., 2007; Gates et al., 2000; Herling et al., 2012). Previous experimental studies showed that organoclays (e.g., tetramethylammonium modified montmorillonite, TMA-Mt) with lower layer charges always have better adsorption capacity toward HOCs as compared with those with higher layer charges, which has been attributed to the larger specific surface areas for the former samples. In other words, more exposed siloxane surfaces, which have been regarded as the main adsorption sites for HOCs, are available for those samples with lower layer charges (Zhu et al., 2007; Gates et al., 2000; Herling et al., 2012). However, the influence of the charge density on the hydration characteristics of clay mineral has not been well studied yet; and it is not quite clear yet how the charge density influences the hydration characteristics of siloxane surfaces and then their interactions with HOCs.

In the present work, the effects of charge density of clay minerals on the hydration characteristics of their siloxane surface were studied by using molecular dynamics (MD) simulations. The advantage of MD simulations is that clay minerals with desired charge type/density can be conveniently established, and atomic-level insights of the interlayer structure of the hydrated clay minerals can be obtained. Four Mt. models containing different layer charges were created; and their charges were exclusively contributed by octahedral substitutions to exclude the influence of charge types on interlayer hydration. All the charges were compensated with TMA, as it has weaker hydration capacity than most inorganic cations and thus can reduce the effects of interlayer cations on the hydration of siloxane surface. Various amounts of water molecules were added to the interlayer space of montmorillonite to model the different hydration levels.

2. Methodology

2.1. Montmorillonite models

Four Mt. with different layer charges were created by substituting desired amount of Al with Mg in the octahedral sheet. The substitution sites were randomly chosen as far as the Loewenstein's rule was satisfied, i.e., two substitution sites cannot be adjacent (Loewenstein, 1954). The simulation cells were approximately 21, 36, 100 Å for a, b, and c directions, respectively, with the surface parallel to the ab plane and the vacuum in the c direction. The formula of the four Mt. were as follows: $Na_{0.25}Al_{1.75}Mg_{0.25}Si_4O_{10}(OH)_2{\cdot}nH_2O$, $Na_{0.3125}Al_{1.6875}Mg_{0.3125}Si_4O_{10}(OH)_2{\cdot}nH_2O$, $Na_{0.375}Al_{1.625}Mg_{0.375}Si_4O_{10}(OH)_2{\cdot}nH_2O$, and $Na_{0.4375}Al_{1.5625}Mg_{0.4375}Si_4O_{10}(OH)_2{\cdot}nH_2O$. As such, the layer charges of the four Mt. samples are approximately 0.25, 0.31, 0.38, and 0.44 per formula unit, in the typical charge range of Mt. (i.e., 0.2–0.6 per formula unit) (Loewenstein, 1954). Each Mt. slab contains 16 unit cells (4 × 4 × 1) and, therefore, the slabs have 8, 10, 12, and 14 octahedral charged sites, respectively. Two slabs were employed to create the interlayer space for Mt. The TMA-Mt configurations were generated by replacing the Na^+ ions with TMA. Accordingly, TMA-Mt containing different charges and TMA cations were denoted as TMA-8Mt, TMA-10Mt, TMA-12Mt and TMA-14Mt, respectively. As clay minerals are common in soil and sediment, they will face a wide range of water content conditions, while they are presented in the environment with different humidity and in aqueous environment. In this term, various amounts of water molecules (0.3125–5 water molecules per unit cell, or 5–80 water molecules in total) were added to the interlayer space of TMA-Mt to investigate their hydration property with different water contents.

2.2. MD simulations

The MD simulations were run with the DL_POLY_2 code (Smith, 1998). The classical potential modeling based on the Born model was applied for MD simulations. In this model the interaction forces between atoms consist of a long-range Coulombic term supplemented by a short-range potential. The electrostatic interactions are evaluated using Ewald method to a precision of 10^{-5} while the van der Waals interaction cutoff was set to 9.5 Å. Periodic boundary conditions were applied in the three dimensions. The equations of motion were updated using the Verlet-Leapfrog algorithm. The CLAYFF force field (Cygan et al., 2004), the CVFF force field (Dauber-Osguthorpe et al., 1988) and the flexible SPC model (Teleman et al., 1987) incorporated in the CLAYFF force field were applied to Mt., to TMA and to water, respectively. Previous studies have shown that these force fields can be used in combination (Liu et al., 2009; Zhu et al., 2011; Zhou et al., 2012).

All samples were first run for 1 ns in the NPT ensemble (1 bar, 300 K), with a timestep of 1 fs, which were followed by 2 ns simulation in the NVT ensemble (300K). We also performed a 5 ns simulation (NVT ensemble) for TMA-12Mt, and the results showed no obvious difference in comparison with those of 2 ns simulation. Properties such as hydration energy, atom density profiles and molecule mobility were then analyzed using the data from the last 1 ns simulation (NVT ensemble). The atom density profile were calculated by taking the middle of the interlayer space position as the origin of z, the density distribution reads (Zhou et al., 2014):

$$\rho(z) = [N(z\text{-}\Delta z/2, z + \Delta z/2)]/(\Delta z \times S) \tag{1}$$

where $[N(z - \Delta z/2, z + \Delta z/2)]$ is the average number of atoms occurring in the interval of $(z - \Delta z/2, z + \Delta z/2)$ ($\Delta z = 0.3$ Å in this study). The 2-D density profile is calculated by sampling the atom density in three-dimensional space (Crabtree et al., 2013).

3. Results and discussion

3.1. Basal spacing of the samples

The basal spacing of the hydrated montmorillonite can be calculated from the Z-density profiles of surface oxygen atoms (O) of the siloxane surface, which equals to the distance between two corresponding peaks from the adjacent montmorillonite layers (Zhou et al., 2012; Zhu et al., 2012a,b). The obtained results showed that basal spacing was relatively