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Computer simulation of clay-water system: Behaviors of H₂O molecules on kaolin mineral surfaces

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Abstract

Molecular dynamics (MD) simulation is now a popular method in a domain of computational chemistry. It has been applied to many problems on material sciences, earth sciences, biology and so on. It could be applied also to environmental sciences which deal with mineral-organic-water system. Computer simulation is expected to contribute increasingly to environmental sciences in near future. This paper describes introductive works on MD simulation of clay-water system, being aware of possible application to environmental problems in future. Kaolin minerals are well known clay mineral as materials for ceramics and widely occurs in lateritic soils. Here, small scale phenomena in kaolin-water system with size of several-hundred angstroms are focused.

Key Words: Molecular dynamics simulation, Kaolin minerals, Clay-water interaction.

INTRODUCTION

Molecular dynamics (MD) Simulation is one of popular methods in computational chemistry. The computational instruments have been always making great progress. Recent personal computers seems to have too much capability of computation for ordinary jobs. In spite of this great progress, chemists might need the capability much

more. The more powerful the computational capability becomes, the greater the chemists extend computational objects. This situation may bring out new world of computer simulation study on environmental sciences. Such a domain should include complex and large-scaled phenomena. This paper shows MD simulation study of clay-water systems which are somewhat large for MD simulation but too small for environmental sciences. These objects of simulation study is being extended in both of scale and complexity.

This work simulated kaolin minerals, one group of almino-silicates. Their unit layer is composed of one gibbsite sheet and one Si tetrahedral sheet. Interlayer region is bonded by hydrogen bonding between the hydrogen of gibbsite sheet and the oxygen of tetrahedral basal plane.

SIMULATION METHOD

Interatomic potential parameters

Obtaining appropriate interatomic potential parameters is the first step in MD simulation. The simulated system includes kaolin layer and water molecules interacting each other on the layer surface. Interatomic potential model could be regarded as consisting of three parts: potential models of kaolin minerals, of water and of interaction between kaolin and water molecules.

The potential model of kaolin minerals used in this study is derived from a previous work (Shiraki et al. 2002) in which potential parameters were optimized referring an experimental crystal structure (Bish 1993) and I.R. spectra (e.g. Farmer 1974; Johnston et al. 1990; Johnston et al. 1998). The water potential model is modified one based on the KKY model developed empirically by Kumagai et al. (1994). Kaolin-H₂O interaction was determined empirically in this study referring to I.R. spectra of synthesized hydrated phase (Constanzo 1994).

Hydrated phase of kaolin minerals

Kaolin minerals are non-expandable species, not like smectite which is a typical expandable clay mineral. Although smectite expands in wet condition, kaolin minerals have no expandability. Constanzo et al. (1984) synthesized 10 Å hydrated phase of

kaolinite, and found its partially dehydrated 8.6 Å phase. 10 Å phase contains two H₂O molecules per the formula Si₂Al₂O₅(OH)₄ (N=2), and 8.6 Å phase one H₂O molecule (N=1).

In order to investigate expanding properties of kaolin minerals, different numbers of H₂O molecules were intercalated into kaolin structural models. Number of H₂O molecule per the formula Si₂Al₂O₅(OH)₄, assigned by N, was changed in interval of 0.25 up to 4.0. Simulations were carried out with NPT ensemble. Potential energies of interlayer water molecule were averaged for each model with different water content. Structural features of interlayer water were observed in snapshots of relaxed structure.

H₂O adsorption on kaolin surfaces

As kaolin minerals have two different types of surface, it is expected that H₂O adsorption behavior also different on the two sides of layer. Simulation was carried out using a model of hexagonal kaolin unit layer surrounded by H₂O molecules. NTV ensemble was adopted to keep the surrounding space.

RESULTS AND DISCUSSION

Expanding behavior of kaolin minerals

Simulations with different amounts of water were carried out. Figure 1 shows one of those simulated models. Expanding curve of basal spacing against water content

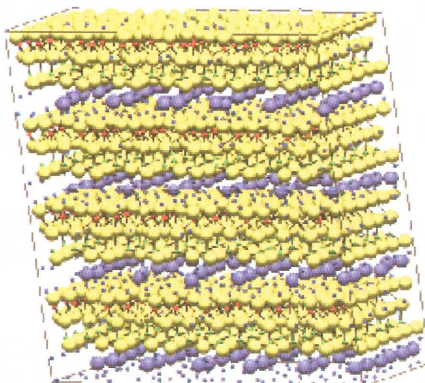


Figure 1 Snapshot of hydrated phase (N=1) in relaxed state with NPT ensemble. The MD basic cell contains four kaolin unit layers and 2692 atoms.

showed irregular step-like pattern. Potential energies for one molecule of interlayer water have minimum at $N=3.0$, which does not correspond to the occurrence of 10 \AA halloysite. But the existence of the minimum is qualitatively concordant to non-expandable character of kaolin minerals.

Structural features of interlayer water are shown in Figure 2 for $N=1$ and $N=2$. Figure 2-a shows regular arrangement of H_2O molecules for $N=1$ (partially dehydrated 8.6 \AA phase). This feature of water molecules corresponds to “hole water” described by Constanzo et al. (1984) and Lipsicas et al. (1985), which is strongly bound to tetrahedral six-membered rings.

Figures 2-b and 2-c show structural relationship of H_2O molecules with tetrahedral sheet for $N=2$ (10 \AA phase). The water molecules are linked by hydrogen bonding each other. There is no “associated water” described by Constanzo et al. (1984) and Lipsicas et al. (1985). This is caused by the stronger water-water interaction than the water-kaolin interaction.

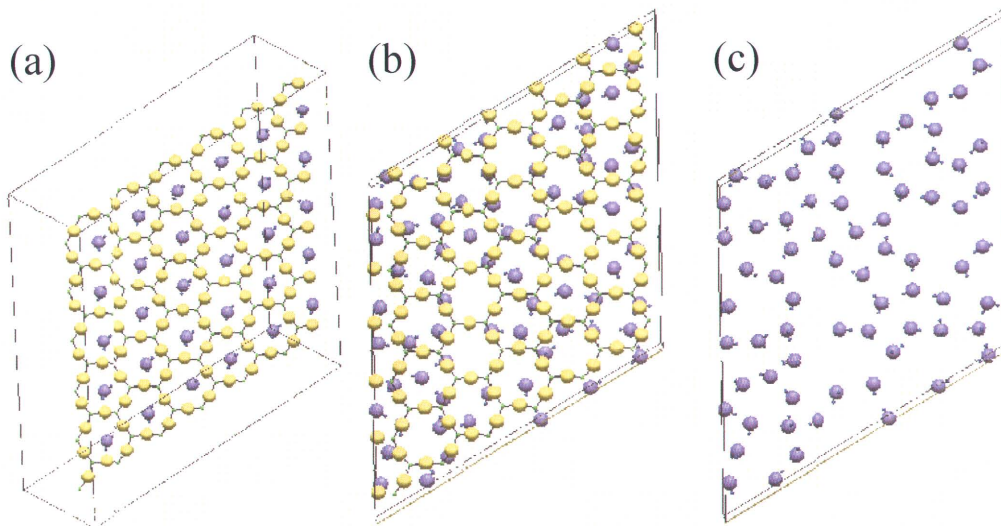


Figure 2 (a) Snapshot of tetrahedral network and interlayer water in relaxed state for $N=1$ (8.6 \AA phase). (b) Same snapshot as (a) for $N=2$ (10 \AA phase). (c) Interlayer water molecules of (b) which seems to tend to form hydrogen bonding between water molecules.

Hydrophilicity of kaolin layer surface

Adsorption behaviors of water molecules on kaolin surfaces were simulated. Figure 3-a shows relaxation process of the MD simulation. In initial state, water

molecules are sparsely distributed around a hexagonal kaolin layer with hydroxyl surface upward (with oxygen surface downward). Starting relaxation, the water molecules flocculate into small drops, then were adsorbed on the kaolin layer.

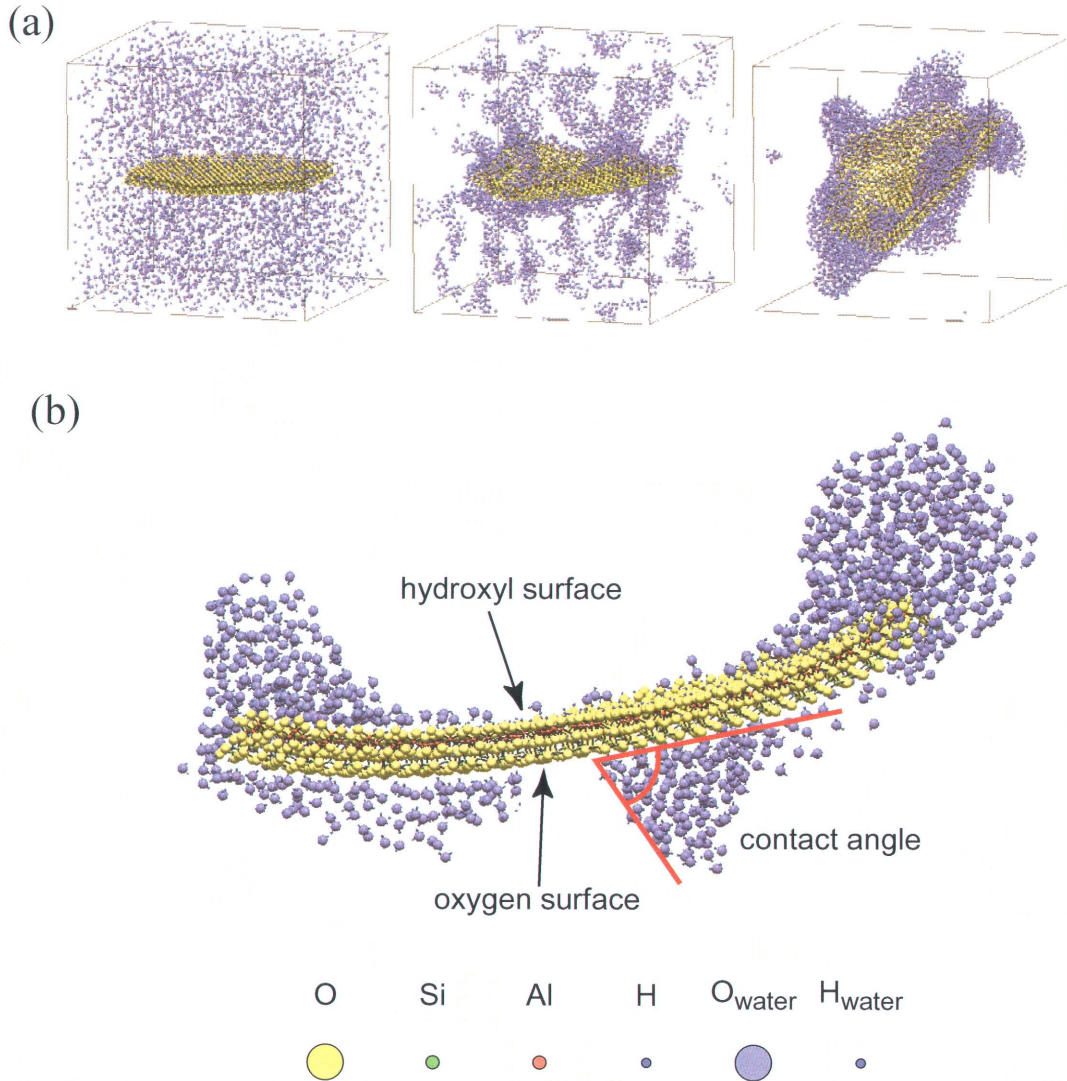


Figure 3 (a) Relaxation process in NTV ensemble, (b) cross section of a snapshot of the relaxed state.

A cross section of adsorbed water on the layer is shown in Figure 3-b. Large area of the hydroxyl surface (upside) is covered by one-molecule layer of H₂O. In contrast, the oxygen surface (downside) has significant uncovered part and high contact angles between the layer and the drop surface. These different adsorption characters implies that the hydroxyl surface is hydrophilic and the oxygen surface is hydrophobic.

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