Variation of properties of smectites in terms of layer charge
- Molecular dynamics simulation study -

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1. Introduction

Smectites are widely distributed in soils, sediments, and sedimentary rocks in the earth's suraface environments. Smectites are also very useful engineering materials because of their remarkable properties. The main properties are adsorption of cations and polar molecules, swelling, dispersion in electlyte solutions, etc. Compositional variations of smectite are significalnt because of the different petrological and geochemical environments. These property are strongly affected by the layer charge of a smectite unit sheet. General formula of beidellite and montmorillonite, two kinds of smectites, can be writen as follows:

beidellite: $Na_x Al_2(OH)_2 [Si_{4-x} Al_xO_{10}].nH_2O$
montmorillonite: $Na_x(Al_{2-x}Mg_x)(OH)_2[Si_4O_{10}].nH_2O$

The layer charge is denoted by $-xe$ in which e is the elementary charge. When the parameter $x=1$, the mineral is margarite, Na variety of dioctahedral mica, whereas x=0 shows a mineral pyrophyllite. Smectite is in the regeon of $0.2<x<0.6$.

2. Interatomic Potential model and Molecular Dynamics Calculations

The Ewald method was used for the summations of Coulomb interactions. Integration of equations of atom motions was performed by the velocity Verlet algorithm with a time increment of 0.4 fs. The NVT (in cases of including vacuum space in the systems) and NPT ensembles were employed, where N is the number of atoms in a periodic cell, V the cell volume, T temperature, and P pressure. Temperature and pressure were controlled by scaling of atom velocities and basic cell edges. Molecular dynamics (MD) simulations were carried out at 293K and 0.1 MPa. The MD simulation codes, MXDORTO and MXDTRICL (Kawamura, 1990-2011) were used. The 100,000 to 2,000,000 step simulations after initial relaxations for each system were carried out to obtain ensemble averaged properties.

The interatomic potential model used in this study is the atom-atom model with full freedom of atom motions [1][2]. The model is composed of two body central force and three body force terms. The two body terms represent Coulomb, van der Waarls, non-bonding short-range repulsive, and radial part of covalent terms in the sequence of following formula, and three body term (only for H-O-H including hydrogen bond) angular part of covalent term.

2 body part:

$$\begin{aligned} u_{ij}(r_{ij}) = {} & \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}} - \frac{c_i c_j}{r_{ij}^{\,6}} + \\ & f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) \\ & + D_{1ij}\exp(-\beta_{1ij} r_{ij}) + D_{2ij}\exp(-\beta_{2ij} r_{ij}) \\ & + D_{3ij}\exp\left[-\beta_{3ij}(r_{ij} - r_{3ij})^2\right] \end{aligned}$$

3 body part:

$$u_{jij}(\theta_{jij}, r_{ij}) = -f_k\{\cos[2(\theta_{jij} - \theta_0)] - 1\}\sqrt{k_1 k_2}$$

$$k_1 = \frac{1}{\exp[g_r(r_{ij1} - r_m)] + 1}$$

The calculation were performd with four compositions of dry beidellite with layer charges, $z=-0.2e$, $-0.333e$, -

0.5e and *-0.6e* respectively. Hydration numbers, $n(H_2O)$ are 0 to 10 in terms of above formula.

3. Results and Discussion

The basal spacings d_{001} and enthalpy of mixing between dry beidellite and water are displayed as functions of hydration number $n(H_2O)$ in Fig.1. The d001-$n(H_2O)$ curves are almost same for the four systems. D001's of hydrated state are slightly small for higher layer charge beidellite. The enthalphy of mixing of dry beidellite and water:

$$\Delta Hmix = H(\text{hydrated beidellite } n(H_2O)) - [H(\text{dry beidellite}) + nH(\text{water})]/(1+n)$$

is also very similar for beidellites of z=0.333e, -0.5 e and -0.6e. The 1 molecular hydration state which is located at the minima near $n(H_2O)$=2.5 shift from $n(H_2O)$=2.5 for *z=-0.2e* to 2.75 for higher layer charge beidellite. The 2 layer hydration states are at $n(H_2O)$=5 or 5.25 for 4 beidellites.

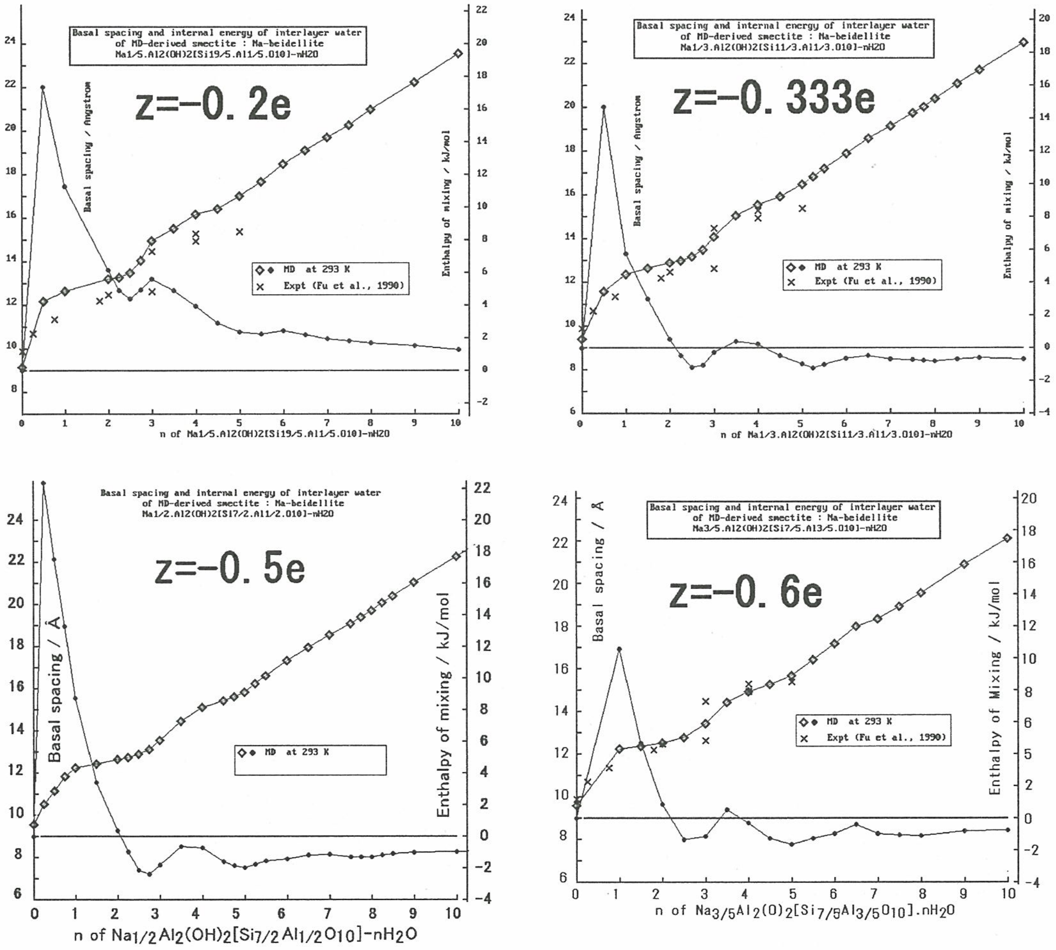

Fig. 1. The basal spacings and entalpy of mixing are plotted against hydration number n(H2O) for four hydrated beidellite.

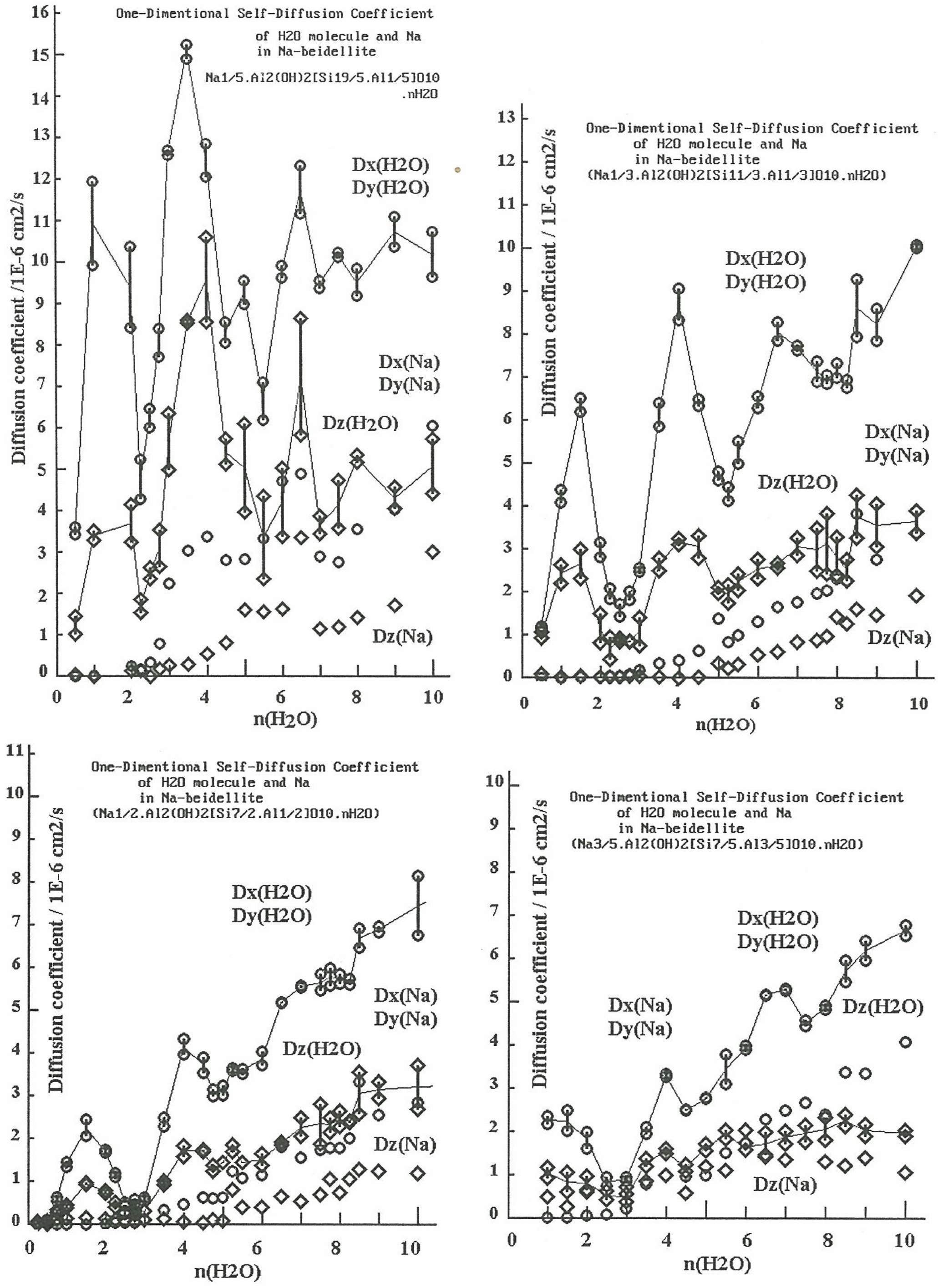

Fig.2. One dimensional self-diffusion coefficients, Dx, Dy and Dz of H2O (circle) molecule and Na ion (dia) are plotted for four hydrated beidellite. The pair of Dx and Dy are connected by vertical lines.

We calculated self diffusion coefficient of interlayer H2O molecule and Na ion using the slope of mean square displacements of the chemical species.

$$D = \frac{1}{6}\frac{d}{d\tau}\left\langle \left[r(t_0) - r(t_0 + \tau) \right]^2 \right\rangle$$

Actually, we are interested in diffusions parallel to a smectite sheet structure. One dimentinal diffusion coefficients can be calculated using the specified coordinate:

$$D_x = \frac{1}{2}\frac{d}{d\tau}\left\langle \left[x(t_0) - x(t_0 + \tau) \right]^2 \right\rangle$$

The calculated one dimensional self-diffusion coefficients of H_2O molecule and Na ion were plotted against hydration number n(H_2O) for each layer charge systems (Fig. 2). The minima of diffusion coefficients correspond to the minima of the enthalpy of mixing in Fig.1. Respectively. The whole shape of graphs are quite different between z=-0.2e and -0.6e systems, and the change is continuous woth the layer charge. The diffusion coefficients of H_2O molecule and Na ion are listed for four layer charge systems in Table 1. The trend of the change can be seen that the large to small diffusivity with the layer charge. The coefficient of low layer chage is larger than that of high layer charge by a few times.

4. Conclusion

The swelling properties and self-diffusion coefficient of interlayer H_2O and Na ion were investigated by means of molecular dynamics simulations. The difference of diffusion coefficient is about twice to three times. The difference is obviously significant for the estimation of the mobility of water and cations. We are carring out further MD calculations to obtain quantitative self-diffusion coefficients.

5. REFERENCES

[1] Naoki KUMAGAI, Katsuyuki KAWAMURA, and Toshio YOKOKAWA (1994) An interatomic potential model for H_2O systems and the molecular dynamics applications to water and ice polymorphs. Molecular Simulation, Vol.12(3-6), 177-186 (1994)

[2] Masashi NAKANO, Katsuyuki KAWAMURA, and Yasuaki ICHIKAWA (2003) Local structural information of Cs in smectite hydrates by means of an EXAFS study and molecular dynamics simulations Applied Clay Science 23 15-23 (2003)

Table 1. One dimensional diffuion coefficients of interlayer H_2O and cation(Na).

	Diffusion coefficient: Dx and Dy / cm^2/s			
	2 molecular layer hydration (n=5)		3 molecular layer hydration (n=7.5)	
	Na	H_2O	Na	H_2O
z=-0.2e	4.0E-6 – 6.1E-6	9.0E-6 – 9.1E-6	3.6E-6 – 4.7E-6	1.0E-6 - 1.1E-5
z=-0.333e	2.0E-6 – 2.01-6	4.6E-6 – 3.5E-6	2.5E-6 – 2.8E-6	6.9E-6 – 7.4E-6
z=-0.5e	2.8E-7 – 4.5E-7	8.9E-8 – 5.3E-7	1.9E-6 – 2.8E-6	5.5E-6 - 5.9E-6
z=-0.6e	1.6E-6 - 1.7E-6	2.8E-6 – 2.8E-6	1.8E-6 – 2.2E-6	4.5E-6 - 4.6E-6