Diffusion of H2O and cations in solution and clays by means of molecular dynamics simulation

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1. Introduction

Smectite clays are the most potential candidates for the engineering barrier of high level radioactive waste. The physical and chemical properties of the materials show extreme advantages for the purpose in terms of the required capability. However, the prediction of the properties for long term behavior is not easy because of the very fine complex materials. We have studied the nano-properties using molecular dynamics methods which solve the equation of motions of atoms and molecules in systems and yield the time dependent coordinates of all the particles in the system. We can calculate a variety of properties using the coordinates. In this study, we show a short sketch of our molecular dynamics simulations and the results of diffusivity of H2O molecules and exchangeable cations in aqueous solutions, interlayer region and surface of clay minerals.

2. Interatomic Potential model and Molecular Dynamics Calculations

The Ewald method was used for the summations of Coulomb interactions. Integration of equation 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, 1990-2009) 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, (Kumagai et al., 1994, Nakano et al., 2003). 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 repulsive, and radial covalent terms in the sequence of following formula, and three body term angular covalent.

3. Self-diffusion in water and aqueous solution

The self diffusion coefficient of water is systematically small compared with experimental one (Fig. 1). At high temperature around 100°C, The relative difference is small. The diffusion coefficients in aqueous solutions also calculated and the behavior ware reproduced well.

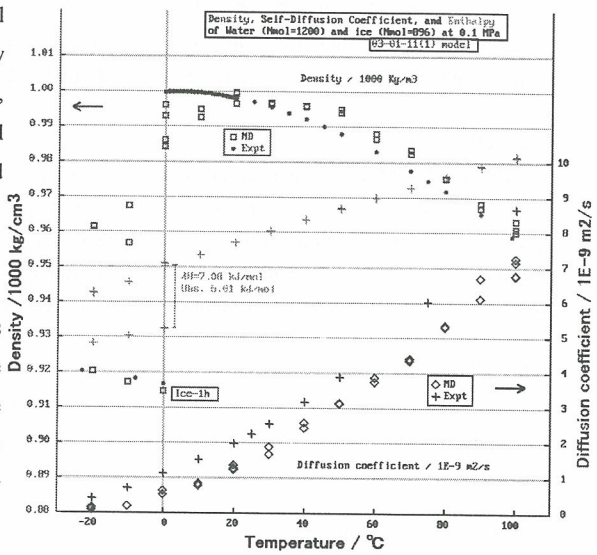

Fig 1. MD results of water and ice Ih

4. Self-diffusion in Interlayer region in beidellite

The two dimensional diffusion coefficients ware calculated for H_2O and exchangeable cation in interlayer region of beidellite (layer charge=0.5e):

$$Na_{0.5}Al_{2}(OH)_{2}[Si_{3.5}Al_{0.5}O_{10}]\text{-}nH_{2}O$$

The diffusion coefficients increase with n of n(H_2O) in the chemical formula. The three minima were seen at n(H2O)=2.5, 5 and 7.5 which correspond to one, two and three molecular layer hydration states.

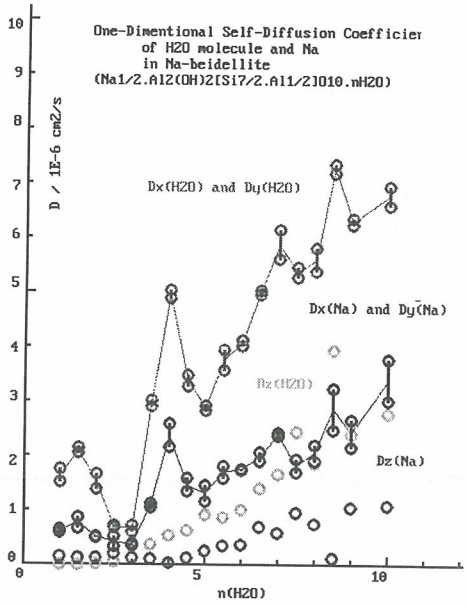

Fig.2 Diffusion coefficients of H2O and exchangeable cation in interlayer

5. Self-diffusion on mineral surfaces

Diffusion coefficients of H_2O in inter particle water was calculated as a function of distance from clay mineral surface. The diffusivity decrease and the viscosity increase near the clay mineral surface.

6. Conclusion

We have developed the molecular simulation method for clay mineral–water systems. The local diffusivity and viscosity were effectively derived using molecular dynamics methods and our interatomic potential model. These data are used in the micro-macro mechanical analyses (Ichikawa, this session).

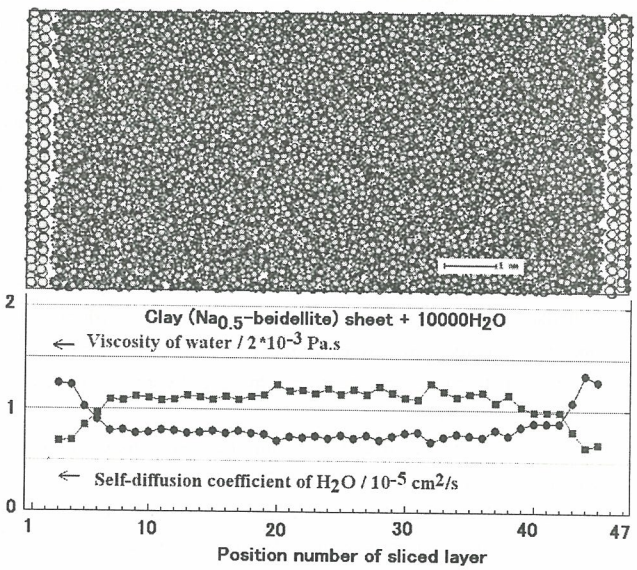

Fig.3 Structure, Diffusion coefficient and viscosity of H2O on clay mineral surface

REFERENCES

[1] N.Kumagai, K.Kawamura, K. and T.Yokokawa, T., Molecular Simulation 12, pp177- 186 (1994).

[2] M.Nakano, K.Kawamura and Y.Ichikawa, Applied Clay Science 23, pp15-23 (2003).