

EFFECTS OF CLAY FRACTION AND TEMPERATURE ON THE H₂O SELF-DIFFUSIVITY IN HECTORITE GEL: A PULSED-FIELD-GRADIENT SPIN-ECHO NUCLEAR MAGNETIC RESONANCE STUDY

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Abstract—Self-diffusion coefficients of H₂O molecules in Na-rich hectorite gel were measured by ¹H nuclear magnetic resonance (NMR). Spin-echo pulse sequences with magnetic field gradient pulses for the translational diffusion measurement were applied to the hectorite gel at the Larmor frequency of 20 MHz. Effects of clay fraction (0–51.2 wt. %) and temperature (20.0–60.3°C) were studied. The results show: (1) Phenomenologically, the self-diffusion coefficient, *D*, of ¹H₂O in the clay gel is expressed by the normalized diffusivity, $D/D_0 = \exp(-0.0257w)$, where *D*₀ is the water self-diffusivity in bulk water at temperature and *w* is the weight fraction of the hectorite (wt. %). (2) The activation energy of H₂O diffusivity in the hectorite gel is nearly equal to that in bulk water. Hence, the normalized diffusivity, *D*/*D*₀, obeys a temperature-independent curve. (3) The exponential dependence of *D*/*D*₀ on *w* for *w* < 30 wt. % is explained by a random-walk model, in which free or unbound H₂O molecules migrate in the geometrically complex and tortuous pore structure of randomly scattered clay-mineral grains.

Key Words—Complexity of Pore Structure, Hectorite, H₂O, NMR, Self-Diffusion.

INTRODUCTION

Diffusion is a dominant mechanism of ground-water migration through less permeable clay barriers with small Péclet values. Thus, measurements of the coefficients of diffusion of H₂O in clay are important in applied clay science, particularly for nuclear waste disposal (e.g., Madsen, 1998). Many studies exist on H₂O mobility or diffusivity in clays (e.g., Mokady and Low, 1968; Low, 1976, 1979; Cebula *et al.*, 1981; Fripiat *et al.*, 1984; Tuck *et al.*, 1985; Miyahara *et al.*, 1991; Sato *et al.*, 1992; Chang *et al.*, 1995, 1998; Yu and Neretnieks, 1997; Ichikawa *et al.*, 1999). One of the most important results of these studies is that H₂O diffusivity in clay depends on the water fraction. For example, Cebula *et al.* (1981) and Chang *et al.* (1995, 1998) argued that diffusivity increases with increasing water fraction for relatively dry (<30 wt. % H₂O) clay. However, an extensive study on the effects of clay or water fractions on H₂O diffusivity has not been made for a clay gel of >50 wt. % H₂O, which is more relevant to nuclear waste disposal because clay below the ground-water level contains significant amounts of water. In the present study, systematic experiments on H₂O diffusion were performed for hectorite (a common clay mineral) gel of >48.8 wt. % H₂O at five sample temperatures.

The self-diffusion coefficients of water molecules (¹H₂O) in a Na-rich hectorite gel were measured using spin-echo ¹H nuclear magnetic resonance (NMR). The pulsed-field-gradient (PFG) proton NMR technique is appropriate to obtain high-precision data on the translational diffusivity of H₂O in clay (Fripiat *et al.*, 1984; Nakashima *et al.*, 1999). This technique was applied in the present study (1) to examine the effects of the

clay weight fraction of the gel on the self-diffusion coefficients of ¹H₂O molecules and (2) to evaluate the temperature-dependence of self-diffusivity. The obtained diffusion data were analyzed by a random-walk model of unbound H₂O molecules in porous media.

EXPERIMENTAL METHODS

Hectorite is a trioctahedral smectite. The ideal formula of Na-rich hectorite is (Mg_{3-y}Li_y)Si₄O₁₀(OH)₂Na₂·*n*H₂O (*y* = 0.2–0.6). The negative charge of the silicate layer is derived from the substitution of Li⁺ for Mg²⁺ in the octahedral sheet. The Na-rich hectorite sample used is a synthetic powder produced by Kunimine Industries Co., Ltd (Tokyo, Japan). The chemical composition (wt. %) is: SiO₂, 49.92; Al₂O₃, 0.04; MgO, 24.3; Li₂O, 0.99; CaO, 0.12; Na₂O, 5.59; SO₃, 0.97; and H₂O, 18.03 (total 99.96). This Mn- and Fe-free synthetic sample is essential to the high-precision NMR experiments because paramagnetic impurities shorten relaxation times of protons. The weight loss of the powder sample was 8.5 wt. % at 110°C. The average grain diameter of the hectorite in suspension (0.2 wt. % clay) was found to be 0.054 μm by the laser-Doppler method.

By adding deionized water to the powder sample, 20 clay-gel samples (ranging from 1.83 to 51.2 wt. % clay) were prepared. The self-diffusion coefficient in bulk water (deionized water) was also measured at 25, 35, and 45°C to determine the accuracy of the NMR data. Relaxation times (*T*₁, spin-lattice relaxation time, and *T*₂, spin-spin relaxation time) for protons associated with H₂O of the 20 gel samples and deionized water were measured at 39.7°C (Figure 1; Table 1). The bulk densities of the 21 samples at 22°C were

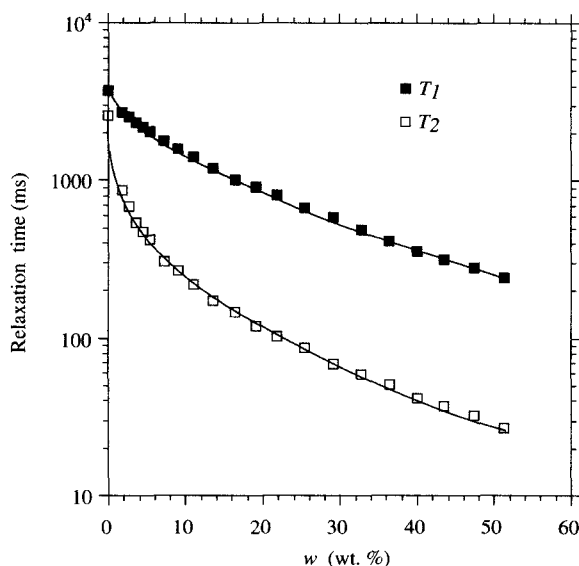


Figure 1. Relaxation times of protons in hectorite gel at 20 MHz and 39.7°C versus clay fraction, w (data from Table 1). T_1 and T_2 were measured by the inversion recovery method and spin-echo method, respectively. The 90°–180° pulse separation was 0.5 ms for the spin-echo method. The solid lines were approximated.

obtained by weighing each sample of known volume (Table 1).

Self-diffusion coefficients were calculated by measuring the decrease in the NMR-signal intensity with increasing magnetic field gradients (Stejskal and Tanner, 1965). The pulsed-field-gradient (PFG) spin-echo

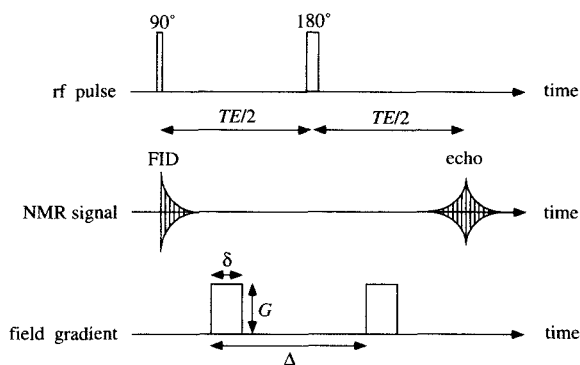


Figure 2. A diffusion-weighted spin-echo pulse sequence used in the present study. A spin-echo NMR signal is generated from a sequence consisting of 90° and 180° radio-frequency (rf) pulses and the intensity is modulated by two field-gradient pulses. A 90° pulse refers to a pulse which rotates the magnetization vector of protons by 90°. TE is the echo time. This sequence is repeated at a period of TR . FID is a free induction decay signal which was not measured in the present study.

pulse sequence used is shown in Figure 2. The NMR spin-echo signal intensity, I , is given by:

$$I = I_0 \exp(-bD) \quad (1)$$

where

$$b = (\gamma G \delta)^2 (\Delta - \delta/3). \quad (2)$$

The quantity I_0 is the signal intensity without magnetic field gradients, γ is the gyromagnetic ratio of a proton (2.675×10^8 rad/Ts), G is the strength of the gradient pulses, δ is the duration of the field gradient pulses, Δ

Table 1. Results of the NMR experiments of hectorite gel ($\Delta = 14$ ms). The water fraction (wt. %) is $100 - w$ and includes pre-existing H_2O (weight loss of 8.5 wt. % at 110°C) of the clay powder.

w (wt. %)	Density 22°C (g/mL)	T_1 39.7°C (ms)	T_2 39.7°C (ms)	D					E (kJ/mol)
				20.0°C	30.1°C	(10 ⁻⁷ m ² /s) 39.7°C	50.3°C	60.3°C	
0.00	1.0	3750	2594	1.96	2.55	3.22	4.05	4.86	18.1
1.83	1.0	2718	861	1.86	2.43	3.09	3.86	4.66	18.2
2.74	1.0	2541	682	1.82	2.37	3.00	3.74	4.53	18.1
3.66	1.0	2345	541	1.78	2.30	2.93	3.65	4.42	18.2
4.57	1.0	2180	477	1.73	2.26	2.86	3.59	4.32	18.2
5.48	1.0	2019	420	1.69	2.19	2.79	3.48	4.23	18.3
7.24	1.1	1770	308	1.60	2.09	2.63	3.30	4.00	18.3
9.08	1.1	1586	268	1.54	2.00	2.55	3.18	3.85	18.2
11.0	1.1	1413	217	1.46	1.89	2.41	3.00	3.63	18.2
13.5	1.1	1200	173	1.36	1.77	2.26	2.80	3.41	18.2
16.4	1.2	1015	146	1.258	1.63	2.08	2.59	3.14	18.3
19.1	1.2	909	120	1.17	1.53	1.94	2.43	2.95	18.4
21.8	1.2	815	103	1.11	1.44	1.84	2.29	2.79	18.4
25.4	1.2	674	86.7	1.02	1.34	1.69	2.11	2.58	18.5
29.2	1.2	587	68.6	0.943	1.24	1.56	1.97	2.40	18.6
32.8	1.3	491	58.9	0.869	1.13	1.44	1.82	2.21	18.7
36.5	1.4	415	50.7	0.779	1.01	1.28	1.62	1.97	18.5
40.0	1.4	353	41.6	0.698	0.894	1.14	1.43	1.73	18.3
43.4	1.4	314	37.3	0.683	0.878	1.10	1.39	1.69	18.3
47.4	1.5	281	32.2	0.600	0.729	0.956	1.18	1.44	18.0
51.2	1.6	240	27.1	0.537	0.667	0.859	1.05	1.30	18.0

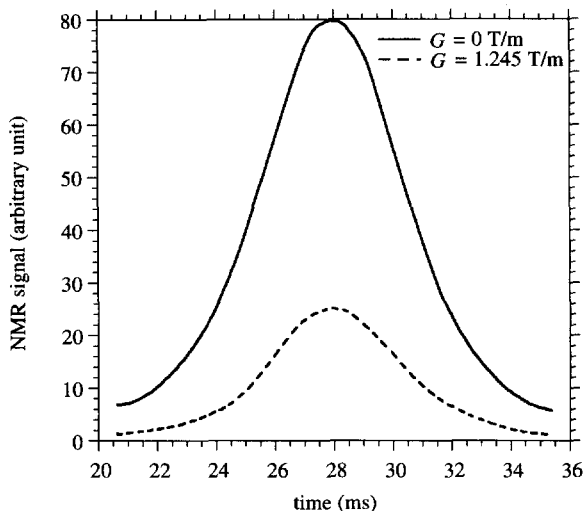


Figure 3. Example of spin-echo NMR signals for $w = 29.2$ wt. % at 39.7°C . The field-gradient intensity is indicated. The echo height at $TE = 28$ ms obeys Equation (1).

is the interval between two gradient pulses (characteristic diffusion time of H₂O molecules), and D is the self-diffusion coefficient of H₂O (e.g., Johnson, 1996).

PFG NMR measurements were performed with an NMS120 proton spectrometer (Bruker, Karlsruhe, Germany) at the resonant frequency of 20 MHz. Each sample (volume ~ 1 cm³) was placed in a separate glass tube (outside diameter, 10 mm). A probehead PH20/10VTS with gradient coils was used to produce magnetic field gradients of ≤ 2.1 T/m. The pulse parameters were as follows: $\delta = 0.7$ ms, the echo time $TE = 28$ ms, $\Delta = 14$ ms, the 90° pulse length was 2.8 μs , and the number of stacking of echo signals was 16. The repetition time of the pulse sequence, TR , was taken to be $TR = 5T_1$. About ten values of G (from 0 to 2.1 T/m) were used for a specific clay fraction and temperature to measure the dependence of I on b . As a result, D was calculated from a regression analysis of the data sets (I/I_0 , b) using Equation (1). The experiments were performed at atmospheric pressure and no pressure vessel (e.g., Figure 1 of Miyahara *et al.*, 1991) was used. Five temperatures (20.0, 30.1, 39.7, 50.3, and 60.3°C) were chosen to calculate the activation energy for the diffusion process.

Because the silicate layer of each clay grain is impermeable, diffusing H₂O molecules are forced to go around the obstacles (clay grains) in the porous gel. Thus, the random-walk trajectory of the molecules is probably restricted by these obstacles, which is termed a 'restricted diffusion regime'. The condition of the regime is $\Delta \gg d^2/6D$ where d is the average pore diameter of the clay gel (e.g., Callaghan, 1991). The physical meaning is that characteristic diffusion time of H₂O (Δ) is much larger than the time required for migrating H₂O to travel a pore of d in size ($d^2/6D$). In

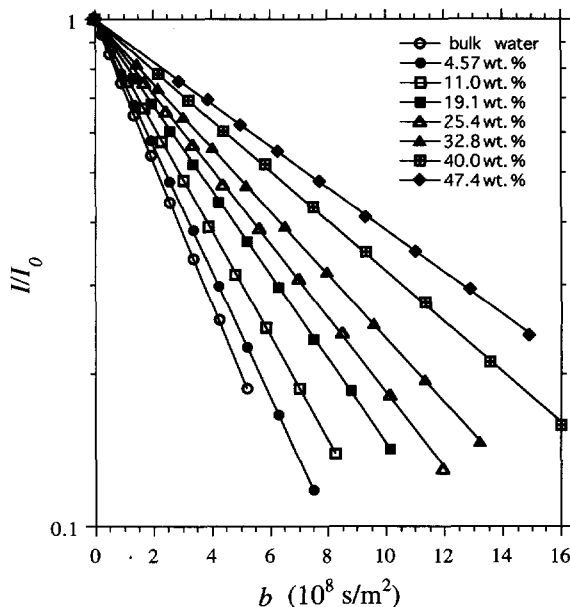


Figure 4. NMR-signal intensities versus the b factor at 39.7°C for eight samples. Each clay fraction is indicated. Data points are fitted to Equation (1) by a least-squares method. Note that higher D yields a higher slope.

terms of the diffusivity, this regime is characterized by Δ -independence of D . Thus, large- Δ experiments ($\Delta = 140$ ms) were also performed for some samples to confirm that the measured H₂O diffusivity was under the restricted diffusion regime.

RESULTS AND DISCUSSION

A qualitative discussion on D is possible using proton relaxation data. Figure 1 shows that T_1 and T_2 decrease as the clay fraction increases. The mechanism for the spin relaxation in porous media is the collision of diffusing H₂O molecules at the surface of solids. The small (or large) T_1 and T_2 imply the high (or low) collision-frequency. The high (or low) collision-frequency is related to the dense (or sparse) packing structure of the clay grains in which H₂O molecules diffuse by a random walk. The dense (or sparse) packing yields the low (or high) values of D because the clay grains are obstacles for the migrating H₂O molecules. Thus Figure 1 predicts that H₂O self-diffusivity decreases with increasing clay fraction. This qualitative prediction is quantitatively verified by the PFG NMR experiments of the present study.

Examples of time domain spin-echo signals (Figure 3) and b -dependent echo intensities (Figure 4) are shown for selected clay samples. The slope of each regression line in Figure 4 gives the self-diffusion coefficient of H₂O, D . These regression lines gave high precision in the calculated diffusion-coefficient values. The accuracy of the PFG NMR experiments can be

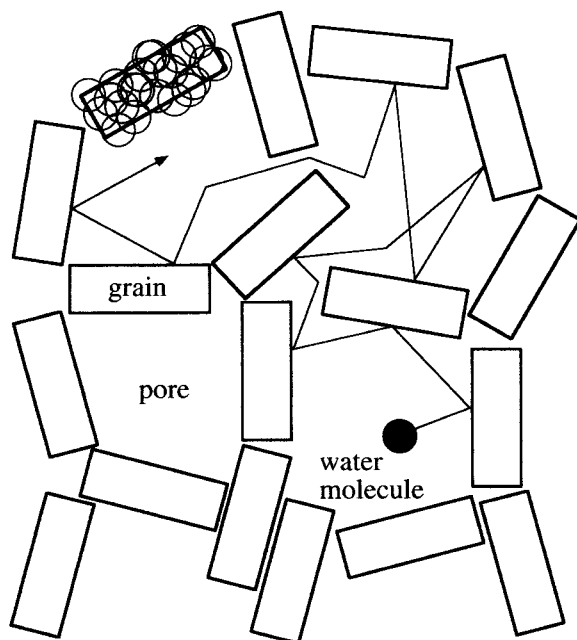


Figure 5. Schematic microstructure of hectorite gel. The trajectory (arrow) of the random walk is geometrically restricted by the packing of hectorite grains. An example of the random covering of clay by circles is shown for a single grain. As w increases, the water-filled pore space may shrink into the interlayer space filled with several monolayers of H_2O between clay platelets.

discussed by using the diffusion coefficient for bulk water (Holz and Weingärtner, 1991). Mills (1973) produced very reliable values for diffusion in bulk water, $D = 2.299 \times 10^{-9} \text{ m}^2/\text{s}$ at 25.0°C , $2.919 \times 10^{-9} \text{ m}^2/\text{s}$ at 35.0°C , and $3.575 \times 10^{-9} \text{ m}^2/\text{s}$ at 45.0°C . The self-diffusivity of the bulk water sample, D_0 , measured here was $2.25 \times 10^{-9} \text{ m}^2/\text{s}$ at 25.0°C , $2.89 \times 10^{-9} \text{ m}^2/\text{s}$ at 35.0°C , and $3.58 \times 10^{-9} \text{ m}^2/\text{s}$ at 45.0°C . These values agree well with the data of Mills (1973), suggesting that the experiments reported here were performed reliably. These bulk-water experiments suggest that the accuracy of the PFG NMR experiments is near $10^{-11} \text{ m}^2/\text{s}$.

The restricted diffusion regime is characterized by the Δ -independence of D . Thus, comparison of the diffusivity obtained by small- and large- Δ experiments was performed to determine that the measured H_2O diffusivity was under the regime. For example, measured D values at 39.7°C for $\Delta = 14 \text{ ms}$ were 2.86, 2.63, and $2.41 \times 10^{-9} \text{ m}^2/\text{s}$ for $w = 4.57, 7.24,$ and $11.0 \text{ wt. } \%$, respectively (Table 1). The values for $\Delta = 140 \text{ ms}$ were 2.84, 2.67, and $2.39 \times 10^{-9} \text{ m}^2/\text{s}$, respectively. They agree well with each other to within error, which suggests that the present NMR experiments are under the fully restricted diffusion regime.

In the restricted diffusion regime, the translational diffusivity is controlled by the complex and tortuous

structure of porous media as shown in Figure 5 (e.g., Latour *et al.*, 1993). The migration distance (root-mean-square displacement) of random walkers in three-dimensional space is $(6D\Delta)^{1/2}$ (e.g., Hollewand and Gladden, 1995). Because $D = 0.5\text{--}5 \times 10^{-9} \text{ m}^2/\text{s}$ (Table 1) and $\Delta = 14 \text{ ms}$, $(6D\Delta)^{1/2}$ is equal to $6\text{--}20 \mu\text{m}$. This characteristic diffusion length in NMR experiments is several orders of magnitude longer than that in molecular-dynamic simulations and neutron-scattering experiments. The measured diffusivity in the regime is a result of a random walk traveling a long distance compared to the pore size, d (e.g., Callaghan, 1991). Therefore, the average pore size of the gel structure of hectorite is $\ll 6\text{--}20 \mu\text{m}$. This may be a unique aspect of clay gel when compared with other gels, for example, polyacrylate (Zeng and Stejskal, 1996), agarose (Pavesi and Balzarini, 1996), and polyacrylamide (Pavesi and Rigamonti, 1995) for which d of a few tens of microns was found. As for the hectorite samples used here, the average grain diameter is $0.054 \mu\text{m}$. Probably the clay-gel pore size is also small (i.e., submicron) because the gel structure is constructed by the packing of the fine grains. Actually, Monma *et al.* (1997) reported pore diameters of $<1 \mu\text{m}$ for $w = 2 \text{ wt. } \%$ hectorite gel as produced by Kunimine Industries using Cryo-SEM (low vacuum scanning electron microscopy for water-rich samples). These results are consistent with the NMR data suggesting that $d \ll 6\text{--}20 \mu\text{m}$. Thus, for example, if $d = 0.5 \mu\text{m}$ and $(6D\Delta)^{1/2} = 10 \mu\text{m}$, then the measured diffusivity by PFG NMR is the diffusivity of H_2O molecules migrating by $\sim 10/0.5 = 20$ pores.

The H_2O self-diffusion coefficients, D , in the hectorite gel as a function of clay weight fraction, w , at various temperatures are shown in Figure 6 and Table 1. At all temperatures examined, D decreases with an increase in w . All D values in the clay are smaller than those in bulk water. At a high w , D is small because the H_2O mobility is strongly restricted by densely packed clay-mineral grains (Figure 5). As w decreases, the density of obstacles (clay grains) for the random walk decreases, and thus H_2O mobility increases. For a sample dominated by H_2O , the H_2O molecules diffuse as if they were in bulk water, and D approaches the diffusivity of bulk water.

A simple phenomenological equation relating w to D is proposed in the present study:

$$D/D_0 = \exp(-\alpha w) \quad (3)$$

where D_0 is the diffusivity for bulk water at temperature, α is a dimensionless constant, and w is a clay weight fraction (in wt. %). Equation (3) satisfies $D = D_0$ at $w = 0 \text{ wt. } \%$. The fitting of Equation (3) to the data is shown in Figures 6 and 7 and each calculated α value is listed in Table 2. Table 2 shows that α is nearly independent of the sample temperature. As a result, a single temperature-independent master curve,

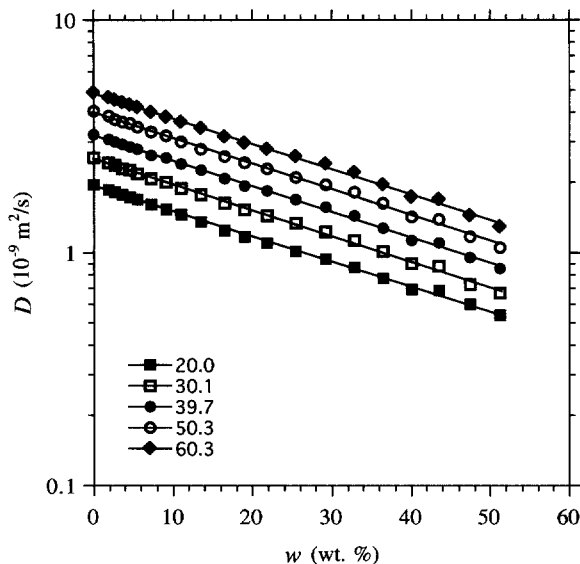


Figure 6. Self-diffusion coefficients of H₂O in hectorite gel, *D*, as a function of clay fraction, *w*, of the gel at various temperatures. Data are from Table 1. Data points are fitted to Equation (3) by a *least-squares* method. Temperatures in °C.

Equation (3), was determined (Figure 7). Low (1979) found that some properties (*e.g.*, viscosity of interlayer H₂O) of montmorillonite/water systems were given by $\exp[cw/(100 - w)]$ where *c* was a numerical constant. The fit of the empirical equation of Low (1979) was

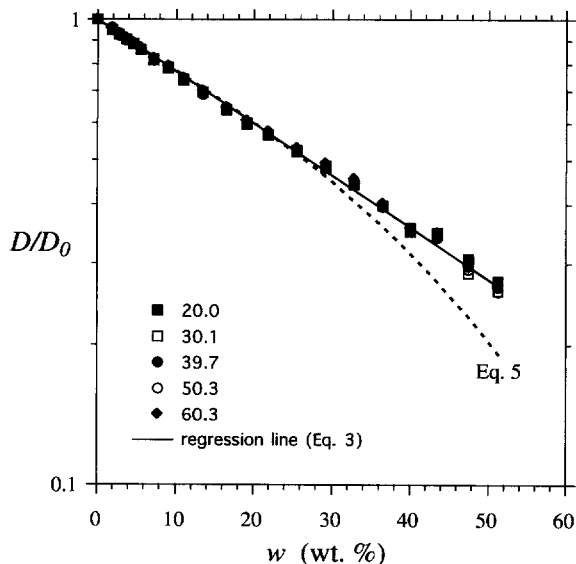


Figure 7. Normalized diffusivity, D/D_0 , (data identical to Figure 6) versus clay fraction, *w*. Data points are fitted to Equation (3) by a *least-squares* method ($\alpha = 0.0257$). Note that the normalized diffusivity is independent of temperature. Equation (5) for $\beta = 7.3$ and $\rho_v/\rho_w = 2.3$ is indicated by a broken curve. Temperatures in °C.

Table 2. Dimensionless parameter, α of Equation (3) in Figure 6 (each temperature) and in Figure 7 (average for all temperatures). Calculated by a *least-squares* method.

Temperature (°C)	α
20.0	0.0257
30.1	0.0259
39.7	0.0256
50.3	0.0259
60.3	0.0253
average	0.0257

applied to the data of Table 1, but the fit is very unsatisfactory.

An Arrhenius plot of the diffusion data (Table 1) is shown in Figure 8. Activation energy, *E*, is calculated from

$$D = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where *A* is a constant, *R* is the gas constant, and *T* is the absolute temperature. The activation energy of bulk water (18.1 kJ/mol; Table 1) for 20.0–60.3°C is nearly equal to the result of Mills (1973) of 17.6 kJ/mol for the temperature range of 15–45°C, which suggests that the NMR experiments were performed in a reliable manner. Whereas the weak non-Arrhenius behavior of bulk water and clay gel was observed for a broader temperature range (2–225°C, Krynicki *et al.*, 1979; 4–55°C, Fripiat *et al.*, 1984), the Arrhenius fitting to Equation (4) in Figure 8 appears reasonable

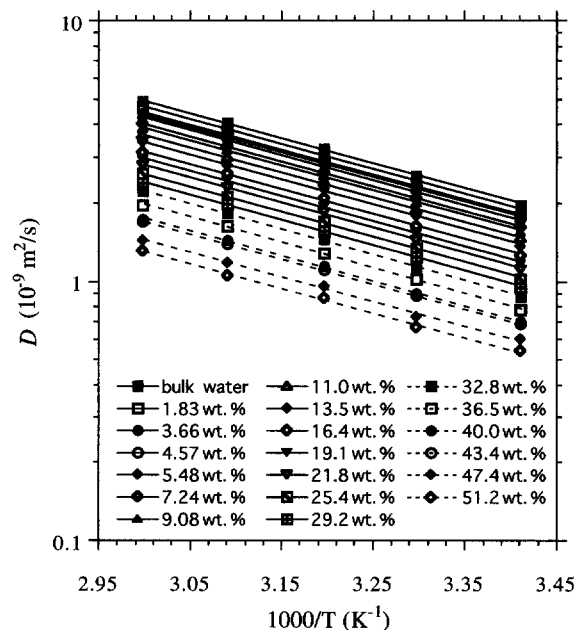


Figure 8. Arrhenius plot of *D* for various clay fractions. The data set is from Table 1. Data points are fitted to Equation (4) by a *least-squares* method.

also, probably because of the narrow temperature range of the present study. Table 1 indicates that the activation energy for each hectorite gel sample nearly equals the value for bulk water. The temperature-independence of D/D_0 in Equation (3) is a consequence of this w -independence of E .

There are two possible reasons for D/D_0 of less than unity for clay gels; bound or less mobile H_2O molecules may occur near negatively charged clay surfaces and/or the geometrical complexity of the pore structure of clay gel through which H_2O molecules migrate by random walk. (1) In the NMR experiments, H_2O molecules travel sufficiently long distances $[(6D\Delta)^{1/2} = 6\text{--}20\ \mu\text{m}]$ to experience the complex pore structure of the gel (Figure 5). Thus the complexity is a possible reason for the low H_2O -diffusivity in clay gel. (2) The activation energy, E , for clay is nearly equal to that for bulk water (Table 1). This suggests that H_2O molecules in the gel are in the same chemical environment as in bulk water, so the effects of structurally ordered H_2O molecules near the clay surface are probably negligible. (3) The contribution of the low mobility of the bound H_2O is negligible for H_2O -rich clay gels (e.g., Kemper *et al.*, 1964; Low, 1976, 1979; McBride, 1994). For example, the average H_2O viscosity in montmorillonite gels of $w < 50$ wt. % is nearly equal to the viscosity of bulk water [Equation (38) of Low, 1979]. This result occurs because the population of bound H_2O is small compared to that of free water for water-rich gel. The viscosity is directly related to the diffusivity by the Stokes-Einstein relation. Hence, the contribution of the bound H_2O to the average diffusivity of H_2O in clay gel is also negligible for $w < 50$ wt. %. On the basis of the above (1–3), H_2O diffusion measured by the present PFG NMR experiments is predominantly controlled not by the bound H_2O but by the geometrical complexity of the hectorite gel structure.

The measured diffusivity in Table 1 is explained by a random-walk model. An exact solution of random walk in porous media under the restricted diffusion regime was determined by Netz and Dorfmueller (1997):

$$\frac{D}{D_0} = e^{-x} + x^2 e^x \int_{2x}^{\infty} \frac{e^{-y}}{y} dy \quad (5)$$

where

$$x = \frac{4\pi r^3}{3} \left(\frac{N}{L^3} \right). \quad (6)$$

The quantity r is the radius of a spherical random walker (~ 0.15 nm for H_2O ; Krynicki *et al.*, 1979), N is the number of obstacles, and L is the system size. In the model, spherical random walkers migrate in three-dimensional space where infinitesimal point obstacles (with density of N/L^3) are randomly placed. Effects of the adsorption of walkers on the obstacles are

neglected, so the only factor decreasing D is the geometrical complexity of the porous media. The average grain diameter, $0.054\ \mu\text{m}$, is much smaller than the characteristic diffusion length of H_2O molecules, $6\text{--}20\ \mu\text{m}$. Thus, despite the plane or two-dimensional shape of clay platelets, this three-dimensional model is relevant. Because clay minerals are not infinitesimal and have finite volume, N is taken to be the number of spheres required to cover all clay grains by the equal spheres of radius r (see Figure 5, this is a 'random covering problem' in mathematics). Therefore $N = 3\beta\phi L^3/(400\pi r^3)$ where ϕ is the volume fraction of hectorite (vol. %) and β is the covering density. The quantity ϕ is related to w : $\phi = 100w/[100\rho_h/\rho_w + (1 - \rho_h/\rho_w)w]$ where ρ_h is the density of hectorite and ρ_w is the density of water. A reasonable value of ρ_h/ρ_w is 2.3 (e.g., Anthony *et al.*, 1995). The numerical constant, β , was calculated by computer simulation as: (number of randomly scattered small equal circles required to cover a large square) \times (area of each circle)/(area of the square). Thus, β was estimated at 5–9. The parameter, β , has statistical ambiguity because the random covering process is stochastic. If ρ_h/ρ_w is equal to 2.3, the fit of Equation (5) to the obtained data is the best fit for $\beta = 7.3$ (Figure 7), which falls in the estimated range of 5–9. Figure 7 indicates that the fit is good, particularly for w of < 30 wt. %. When w increases to approach the percolation threshold, the randomly scattered spheres of radius r occupy nearly all of the three-dimensional space, which isolates the pores (Trinh *et al.*, 2000). This is the reason for the sharp drop of Equation (5) for $w > 30$ wt. %. On the other hand, three-dimensionally connected percolation clusters of the pore space for random walk survive in the real clay-gel system, even for high w , because the clay-mineral packing is not random in dense gel, but packing occurs with a 'card-house' structure. This structure may be the possible reason for the underestimate of D/D_0 by Equation (5) for $w > 30$ wt. %. Except for the underestimate, however, the fit of Equation (5) to the NMR data is good. Thus, unbound H_2O molecules diffuse by avoiding randomly placed clay grains for w of < 30 wt. %.

The random-media model by Netz and Dorfmueller (1997) was successfully applied to the hectorite gel of $w < 30$ wt. %. The gel is characterized by high porosity which allows the approximations that (1) the effects of bound H_2O are negligible and (2) the solid distribution is spatially random. Thus, the model is also applicable to other expandable smectite gels with a high water-fraction. PFG NMR enables us to perform quick, precise, and non-destructive measurements of the H_2O mobility. The NMR technique contributes to the study of probing the porous structure of water-rich smectite gel systems.

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REFERENCES

- Anthony, J.W., Bideaux, R.A., Bladh, K.W., and Nichols, M.C. (1995) *Handbook of Mineralogy*. Mineral Data Publishing, Tucson, Arizona, 904 pp.
- Callaghan, P.T. (1991) *Principles of Nuclear Magnetic Resonance Microscopy*. Oxford University Press, Oxford, 492 pp.
- Cebula, D.J., Thomas, R.K., and White, J.W. (1981) Diffusion of water in Li-montmorillonite studied by quasielastic neutron scattering. *Clays and Clay Minerals*, **29**, 241–248.
- Chang, F.-R.C., Skipper, N.T., and Sposito, G. (1995) Computer simulation of interlayer molecular structure in sodium montmorillonite hydrates. *Langmuir*, **11**, 2734–2741.
- Chang, F.-R.C., Skipper, N.T., and Sposito, G. (1998) Monte Carlo and molecular dynamics simulations of electrical double-layer structure in potassium-montmorillonite hydrates. *Langmuir*, **14**, 1201–1207.
- Fripiat, J.J., Letellier, M., and Levitz, P. (1984) Interaction of water with clay surfaces. *Philosophical Transactions of the Royal Society of London*, **A311**, 287–299.
- Hollewand, M.P. and Gladden, L. F. (1995) Transport heterogeneity in porous pellets-I. PGSE NMR studies. *Chemical Engineering Science*, **50**, 309–326.
- Holz, M. and Weingärtner, H. (1991) Calibration in accurate spin-echo self-diffusion measurements using ¹H and less-common nuclei. *Journal of Magnetic Resonance*, **92**, 115–125.
- Ichikawa, Y., Kawamura, K., Nakano, M., Kitayama, K., and Kawamura, H. (1999) Unified molecular dynamics and homogenization analysis for bentonite behavior: Current results and future possibilities. *Engineering Geology*, **54**, 21–31.
- Johnson, C.S., Jr. (1996) Diffusion measurements by magnetic field gradient method. In *Encyclopedia of Nuclear Magnetic Resonance*, D.M. Grant and R.K. Harris, eds., John Wiley & Sons, New York, 1626–1644.
- Kemper, W.D., Maasland, D.E.L., and Porter, L.K. (1964) Mobility of water adjacent to mineral surfaces. *Soil Science Society of America Proceedings*, **28**, 164–167.
- Krynicky, K., Green, C.D., and Sawyer, D.W. (1979) Pressure and temperature dependence of self-diffusion in water. *Faraday Discussions of the Chemical Society*, **66**, 199–208.
- Latour, L.L., Mitra, P.P., Kleinberg, R.L., and Sotak, C.H. (1993) Time-dependent diffusion coefficient of fluids in porous media as a probe of surface-to-volume ratio. *Journal of Magnetic Resonance*, **A101**, 342–346.
- Low, P.F. (1976) Viscosity of interlayer water in montmorillonite. *Soil Science Society of America Journal*, **40**, 500–505.
- Low, P.F. (1979) Nature and properties of water in montmorillonite-water systems. *Soil Science Society of America Journal*, **43**, 651–658.
- Madsen, F.T. (1998) Clay mineralogical investigations related to nuclear waste disposal. *Clay Minerals*, **33**, 109–129.
- McBride, M.B. (1994) Mobility of small molecules in interlayers of hectorite gels: ESR study with an uncharged spin probe. *Clays and Clay Minerals*, **42**, 455–461.
- Mills, R. (1973) Self-diffusion in normal and heavy water in the range 1–45°. *Journal of Physical Chemistry*, **77**, 685–688.
- Miyahara, K., Ashida, T., Kohara, Y., Yusa, Y., and Sasaki, N. (1991) Effect of bulk density on diffusion for cesium in compacted sodium bentonite. *Radiochimica Acta*, **52/53**, 293–297.
- Mokady, R.S. and Low, P.F. (1968) Simultaneous transport of water and salt through clays: I. Transport mechanisms. *Soil Science*, **105**, 112–131.
- Monma, T., Kudo, M., and Masuko, T. (1997) Flow behaviors of smectite/water suspensions in terms of particle-coagulated structures. *Journal of Clay Science Society of Japan*, **37**, 47–57. (in Japanese with English abstract).
- Nakashima, Y., Mitsumori, F., Nakashima, S., and Takahashi, M. (1999) Measurement of self-diffusion coefficients of water in smectite by stimulated echo ¹H nuclear magnetic resonance imaging. *Applied Clay Science*, **14**, 59–68.
- Netz, P.A. and Dorfmueller, T. (1997) Computer simulation studies of diffusion in gels: Model structures. *Journal of Chemical Physics*, **107**, 9221–9233.
- Pavesi, L. and Balzarini, M. (1996) NMR study of the diffusion process in gels. *Magnetic Resonance Imaging*, **14**, 985–987.
- Pavesi, L. and Rigamonti, A. (1995) Diffusion constants in polyacrylamide gels. *Physical Review E*, **51**, 3318–3323.
- Sato, H., Ashida, T., Kohara, Y., Yui, M., and Sasaki, N. (1992) Effect of dry density on diffusion of some radionuclides in compacted sodium bentonite. *Journal of Nuclear Science and Technology*, **29**, 873–882.
- Stejskal, E.O. and Tanner, J.E. (1965) Spin diffusion measurements: Spin echos in the presence of a time-dependent field gradient. *Journal of Chemical Physics*, **42**, 288–292.
- Trinh, S., Arce, P., and Locke, B.R. (2000) Effective diffusivities of point-like molecules in isotropic porous media by Monte Carlo simulation. *Transport in Porous Media*, **38**, 241–259.
- Tuck, J.J., Hall, P.L., and Hayes, M.H. (1985) Quasi-elastic neutron-scattering studies of intercalated molecules in charge-deficient layer silicates: Part 2-High resolution measurements of the diffusion of water in montmorillonite and vermiculite. *Journal of the Chemical Society Faraday Transactions 1*, **81**, 833–846.
- Yu, J.W. and Neretnieks, I. (1997) Diffusion and sorption properties of radionuclides in compacted bentonite. *SKB Technical Report* (Swedish Nuclear Fuel and Waste Management Co.), **97-12**, 1–98.
- Zeng, L. and Stejskal, E.O. (1996) Characterization of a polypropylene/super-absorbent web by NMR diffusion studies. *Applied Spectroscopy*, **50**, 1402–1407.

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