Self-diffusion of H$_2$O in stevensite gel: effects of temperature and clay fraction

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(Received 3 January 2001; revised 11 April 2001)

ABSTRACT: Self-diffusion coefficients of water molecules (1H2O) in Na-stevensite gel were measured by pulsed-gradient spin-echo (PGSE) proton nuclear magnetic resonance (NMR). The effects of clay fraction (0.00–37.7 wt.%) and temperature (20.0–60.3°C) were studied. The results show: (1) phenomenologically, the H2O self-diffusivity in the clay gel, $D$, is expressed by $D/D_0 = \exp(-0.0198\omega)$, where $D_0$ is the H2O self-diffusivity in bulk water of the temperature and $\omega$ is the clay weight fraction (wt.%). (2) The activation energy of the diffusivity in the stevensite gel is nearly equal to that in bulk water. Thus, the normalized diffusivity, $D/D_0$, obeys a temperature-independent master curve. (3) The exponential dependence of $D/D_0$ on $\omega$ for $\omega < 25$ wt.% (~12 vol.%) can be explained by a random walk model, in which unbound H2O molecules diffuse in the geometrically tortuous pore structure of randomly scattered clay mineral grains. (4) The measured diffusivity can also be explained by a model of unbound H2O diffusing in a polymer network with a specific mesh-size or characteristic interval of the crosslinkage.

KEYWORDS: clay gel structure, NMR, porous media, random walk, water molecule.

The dominant migration mechanism of groundwater in clay-bearing, less permeable strata is ‘random walk’ or diffusion. Thus the H2O diffusivity in clay-water systems is important for geological study of water transport in less permeable materials (e.g. Yu & Neretnieks, 1997; Madsen, 1998). Stevensite is a common clay mineral in the earth’s crust (Randall, 1959; Imai et al., 1970; Seitz et al., 1987). However, measurements of H2O diffusivity have not been performed for stevensite-water systems. In the present work, systematic studies of the effects of the clay weight fraction and temperature on the H2O self-diffusivities in stevensite gel were performed by proton nuclear magnetic resonance (NMR) experiments. NMR with pulsed-field gradients is a powerful technique for measuring non-destructively the H2O diffusivity in porous media (Callaghan, 1991; Latour et al., 1993). The technique is easy to apply to the clay gel because of the long proton relaxation times (Fripiat et al., 1984; Nakashima et al., 1999; Nakashima, 2000a,b, 2001). The self-diffusivity in water-rich (>62.3 wt.% H2O) gel was measured because clay minerals contain significant amounts of water in the real geological environment below groundwater level.

The volume of stevensite expands by incorporating H2O molecules between the silicate layers. The resultant high porosity (as high as 80 vol.% or more) of the clay gel enables the quantitative analysis of the diffusion data using a simple model because the effects of bound H2O molecules near negatively charged clay surfaces are negligible. Theoretical diffusion models for H2O in polymer gel by Netz & Dorfmüller (1997) and Tokita et al. (1996) were applied to the diffusion data obtained to provide insight into the diffusion mechanism.

EXPERIMENTAL

The Na-stevensite sample was a synthetic powder produced by the Kunimine Industries Co., Ltd.
The ideal formula of Na-stevensite is \( \text{Na}_2y\text{Mg}_3\text{CO}_0y\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot n\text{H}_2\text{O} \) for \( y = 0.1/\text{CO}_00.3 \). The chemical composition of the product (wt.%) is: \( \text{SiO}_2 49.23 \), \( \text{Al}_2\text{O}_3 0.04 \), \( \text{MgO} 23.89 \), \( \text{CaO} 0.11 \), \( \text{Na}_2\text{O} 5.99 \), \( \text{SO}_3 1.02 \), and \( \text{H}_2\text{O} 19.67 \) (total 99.95). The loss on ignition of the clay powder was 9.9 wt.% at 110°C.

The average grain diameter of the stevensite in a suspension (0.2 wt.% clay) is 0.042 mm. By adding deionized water to the powder sample, 16 clay gel samples (ranging from 1.80 to 37.7 wt.% clay) were prepared. The spin-lattice relaxation time, \( T_1 \), and the spin-spin relaxation time, \( T_2 \), for \( \text{H}_2\text{O} \) protons of the samples were measured at 39.7°C. The measurement of the bulk density, \( \rho_{\text{bulk}} \), of the 17 samples was performed at 22°C by weighing each sample of known volume.

Self-diffusion coefficients are calculated by measuring the decrease in the NMR signal intensity with increasing magnetic field gradients (Stejskal & Tanner, 1965). In the pulsed-gradient spin-echo (PGSE) pulse sequence used, the NMR signal intensity, \( I \), is given by

\[
I = I_0 \exp(-bD) \tag{1}
\]

where \( b = (\gamma G \delta)^2(\Delta - \delta/3) \). The quantity \( I_0 \) is a signal intensity without magnetic field gradients, \( \gamma \) is the gyromagnetic ratio of a proton

\[\begin{array}{cccccccc}
 w & \rho_{\text{bulk}} & T_1 & T_2 & D & D & D & D & E \\
\text{(wt.%)} & 22°C & 39.7°C & 39.7°C & 20.0°C & 30.1°C & 39.7°C & 50.3°C & 60.3°C & \text{(kJ/mol)} \\
0.00 & 1.0 & 3750 & 3279 & 1.95 & 2.55 & 3.23 & 4.07 & 4.88 & 18.2 \\
1.80 & 1.0 & 2783 & 429 & 1.87 & 2.44 & 3.09 & 3.85 & 4.67 & 18.2 \\
3.60 & 1.0 & 2292 & 254 & 1.81 & 2.34 & 2.99 & 3.70 & 4.52 & 18.3 \\
5.40 & 1.1 & 1967 & 180 & 1.72 & 2.25 & 2.85 & 3.56 & 4.32 & 18.2 \\
7.17 & 1.1 & 1724 & 140 & 1.67 & 2.18 & 2.76 & 3.45 & 4.18 & 18.3 \\
8.97 & 1.1 & 1534 & 115 & 1.62 & 2.11 & 2.67 & 3.33 & 4.06 & 18.3 \\
10.8 & 1.1 & 1341 & 95.0 & 1.57 & 2.04 & 2.59 & 3.24 & 3.92 & 18.2 \\
13.5 & 1.1 & 1142 & 76.2 & 1.51 & 1.95 & 2.47 & 3.08 & 3.75 & 18.2 \\
16.2 & 1.2 & 981 & 61.2 & 1.44 & 1.86 & 2.34 & 2.95 & 3.59 & 18.3 \\
18.9 & 1.2 & 851 & 51.1 & 1.37 & 1.78 & 2.24 & 2.79 & 3.39 & 18.1 \\
21.6 & 1.2 & 743 & 42.9 & 1.29 & 1.66 & 2.11 & 2.63 & 3.20 & 18.3 \\
24.2 & 1.2 & 660 & 37.4 & 1.23 & 1.60 & 2.01 & 2.51 & 3.05 & 18.1 \\
26.9 & 1.2 & 593 & 32.1 & 1.16 & 1.51 & 1.90 & 2.38 & 2.89 & 18.2 \\
29.7 & 1.3 & 503 & 27.1 & 1.08 & 1.42 & 1.80 & 2.21 & 2.68 & 17.9 \\
32.4 & 1.3 & 481 & 25.4 & 1.05 & 1.36 & 1.73 & 2.15 & 2.61 & 18.2 \\
35.1 & 1.3 & 425 & 21.9 & 1.00 & 1.27 & 1.62 & 2.01 & 2.44 & 17.9 \\
37.7 & 1.4 & 365 & 18.2 & 0.925 & 1.20 & 1.52 & 1.87 & 2.25 & 17.6 \\
\end{array}\]

(\( \rho_{\text{bulk}} \) in g/ml, \( T_1 \) and \( T_2 \) in ms, \( D \) in \( 10^{-9}\text{m}^2/\text{s} \)). The water fraction (wt.%) is 100 – \( w \) and includes pre-existing \( \text{H}_2\text{O} \) (weight loss of 9.9 wt.% at 110°C) of the clay powder.

![Figure 1](URL) Relaxation times of protons in stevensite gel at 20 MHz and 39.7°C vs. 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° to 180° pulse separation was 0.5 ms for the spin-echo method. The solid lines were approximated.

TABLE 1. Results of the NMR experiments of stevensite gel (\( \Delta = 14\text{ ms} \)). The water fraction (wt.%) is 100 – \( w \) and includes pre-existing \( \text{H}_2\text{O} \) (weight loss of 9.9 wt.% at 110°C) of the clay powder.
(2.675 \times 10^8 \text{ rad/Ts}), \ G \ is \ the \ strength \ of \ the \ gradient \ pulses, \ \delta \ is \ the \ duration \ of \ the \ field \ gradient \ pulses, \ \Delta \ is \ the \ interval \ between \ two \ gradient \ pulses \ (characteristic \ time \ of \ diffusion), \ and \ D \ is \ the \ self-diffusion \ coefficient \ of \ H_2O \ (e.g. \ Callaghan, 1991).

The PGSE NMR measurements were performed at the resonant frequency of 20 MHz and atmospheric pressure using an NMS120 proton spectrometer made by Bruker GmbH. Each sample (volume, 1 cm$^3$) was placed in a separate glass tube (outside diameter, 10 mm). The pulse parameters were as follows: $\delta = 0.7$ ms, the echo time $TE = 28$ ms, $\Delta = 14$ ms, the 90$^\circ$ pulse length was 2.8 $\mu$s, and the number of echo signals stacked was 16. The repetition time of the pulse sequence, $TR$, was taken to be $TR = 5T_1$ (full relaxation condition).

About ten values for $G$ (from 0 to 2.1 T/m) were used for a specified 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. Five temperatures (20.0, 30.1, 39.7, 50.3 and 60.3$^\circ$C) were chosen to observe the temperature-dependence of the diffusivity. Large-$\Delta$ experiments ($\Delta = 100$ ms) were also carried out for some samples to confirm that the measured H$_2$O diffusivity was under the restricted diffusion regime. The self-diffusivity of a bulk water sample was measured at 25.0, 35.0 and 45.0$^\circ$C to check the accuracy of the NMR experiments. The measured diffusivities of the bulk water were compared with the literature data (Mills, 1973) showing that the accuracy was of the order of $10^{-11}$ m$^2$/s.

![FIG. 2. Normalized NMR signal intensities vs. the b factor at 50.3°C for eight samples. $\Delta = 14$ ms. Each clay fraction is indicated. Data points are fitted to equation 1 by a least squares method.](image-url)
Fig. 3. Water self-diffusivities, $D$, in the bulk water and 16 stevensite gel samples. Data are from Table 1 and fitted by a least squares method. (a) $D$ as a function of clay weight fraction at five temperatures (temperatures in °C). The fitted parameter, $\alpha$ of equation 2 is indicated. (b) Arrhenius plot of $D$ for various clay fractions. The data set used is identical to (a).
RESULTS AND DISCUSSION

All experimental results including $T_1$, $T_2$, $D$, $\rho_{\text{bulk}}$ and calculated activation energy are listed in Table 1. The relaxation time decreases with increasing clay weight fraction, $w$ (Fig. 1). The proton relaxation is due to the collision of diffusing $\text{H}_2\text{O}$ molecules with the surfaces of clay minerals (Kleinberg & Vinegar, 1996). Thus, Fig. 1 suggests that the $\text{H}_2\text{O}$ diffusivity also decreases with increasing $w$ (Nakashima, 2000a, 2001). This qualitative prediction is verified quantitatively by the PGSE NMR experiments below.

Examples of $b$-dependent echo intensities (Fig. 2) are shown for some samples. The clear regression lines yield high precision in the calculated diffusion coefficient values. Comparison of the diffusivity obtained by small- and large-$\Delta$ experiments was performed to confirm that the measured $\text{H}_2\text{O}$ diffusivity was under the restricted diffusion regime. The regime is characterized by the $\Delta$-independence of $D$ (e.g. Callaghan, 1991). For example, measured $D$ values at 39.7°C for $\Delta = 14$ ms were 2.99 and $2.24 \times 10^{-9}$ m$^2$/s for $w = 3.60$ and 18.9 wt.%, respectively (Table 1). Those for $\Delta = 100$ ms were 2.93 and $2.27 \times 10^{-9}$ m$^2$/s, respectively. They agree well with each other 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 (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. Callaghan, 1991). Because $D = 0.925 - 4.67 \times 10^{-9}$ m$^2$/s (Table 1) and $\Delta = 14$ ms, $(6D\Delta)^{1/2}$ is equal to $9 - 20$ μm. For the stevensite samples used here, the average grain diameter is 0.042 μm. The clay-gel pore-size is also as small as submicron because the gel structure is constructed by the packing of the fine grains. Hence, for example, if the pore-size is 0.03 μm and $(6D\Delta)^{1/2} = 9$ μm, then the measured diffusivity by PGSE NMR is the diffusivity of $\text{H}_2\text{O}$ molecules migrating by $\sim 9/0.03 = 300$ pores. The above-mentioned $\Delta$-independence of $D$ is a reasonable consequence of the fact that the pore-size is much smaller than $(6D\Delta)^{1/2}$.

![Fig. 4. Random walk model of water in clay gel. A spherical random walker (water molecule, open circle) with radius $r$ is made to go around the randomly placed point obstacles (stevensite grains, solid point) to diffuse. The trajectory (arrow) of the random walk is thus geometrically restricted by the packing of stevensite grains. Each point obstacle has an excluded volume (shaded) with radius $r$ where the centre of gravity of the random walker cannot invade.](image-url)
Water self-diffusion coefficients, $D$, in the stevensite gel as a function of clay weight fraction, $w$, are shown in Fig. 3a. At high $w$, $D$ is small because the H$_2$O mobility is strongly restricted by densely packed clay mineral grains. As $w$ decreases, the density of obstacles (clay grains) for the random walk decreases, so that the H$_2$O mobility increases. A phenomenological exponential formula (Nakashima, 2000a) relating $w$ to $D$ is applicable in the present study:

$$\frac{D}{D_0} = \exp(-\alpha w)$$  \hspace{1cm} (2)

where $D_0$ is $D$ for bulk water at the temperature, $\alpha$ is a dimensionless constant, and $w$ is in wt.\%. This empirical equation was found for hectorite gel (Nakashima, 2000a). The fitting of equation 2 to the data is shown in Figs 3a and 5. Figure 3a indicates that $\alpha$ is nearly independent of the sample temperature. As a result, a single temperature-independent master curve (equation 2) was determined.

An Arrhenius plot of the diffusion data is shown in Fig. 3b. The activation energy, $E$, was calculated from $D = A \exp(-E/RT)$, where $A$ is a constant, $R$ is the gas constant, and $T$ is the absolute temperature. The calculated activation energy of bulk water (18.2 kJ/mol; Table 1) for 20.0–60.3°C is almost equal to the literature data of 17.6 kJ/mol for the temperature range of 15 to 45°C (Mills, 1973), which suggests that the PGSE NMR

![Graph](image.png)

Fig. 5. Normalized diffusivity vs. clay weight fraction (data are identical to Fig. 3). Temperatures in °C. Data points are fitted to equation 2 by a least squares method to obtain $\alpha = 0.0198$ (solid line). Equation 3 for $\beta = 6.2$ and $\rho_s/\rho_w = 2.5$ is indicated by a broken curve. With the assumption that $\rho_s/\rho_w = 2.5$, $w$ is converted into the clay volume fraction, $\phi$. 

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experiments were carried out in a reliable manner. All 17 \( E \) values in Table 1 fall in a narrow range (17.6–18.3 kJ/mol) indicating that \( E \) for the all stevensite gel samples nearly equals that for bulk water. The temperature-independence of \( D/D_0 \) in equation 2 is a consequence of this \( w \)-independence of \( E \).

The diffusion data obtained are explained by a theoretical random walk model. Effects of bound or less mobile H\(_2\)O molecules near negatively charged clay surfaces are negligible for water-rich (i.e. \( w < 50 \) wt.%) clay gels (Low, 1979). Thus the H\(_2\)O diffusion measured by the present experiments is predominantly controlled not by the bound water but by the geometrical tortuosity of the stevensite gel structure. An analytical solution for unbound molecules diffusing in porous media under a restricted diffusion regime was found by Netz & Dorfmüller (1997):

\[
\frac{D}{D_0} = e^{-x} + x^2 e^{-x} \int_{2x}^{\infty} \frac{e^{-y}}{y^2} dy
\]

where \( x = 4\pi r^3 N/(3L^3) \). The quantity \( r \) is the radius of a spherical random walker (\( \approx 0.15 \) nm for H\(_2\)O [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 (number density is \( N/L^3 \)) are randomly placed (Fig. 4). Effects of bound H\(_2\)O near negatively charged clay surfaces are ignored in equation 3. Thus the unique factor controlling the diffusivity is the geometrical complexity of the porous media. Because clay minerals are not infinitesimal but have finite volume, \( N \) is taken to be the number of spheres needed to cover all clay grains by equal spheres of radius \( r \). This is a covering problem in mathematics (Fejes Tóth, 1972). Therefore \( N = 3\phi L^3/(400\pi r^3) \) where \( \phi \) is the volume fraction of stevensite particles (vol.%). The quantity \( \phi \) is related to \( w \): \( \phi = 100w/[100\rho_s/\rho_w - (1 - \rho_s/\rho_w)w] \) where \( \rho_s \) is the grain density of stevensite and \( \rho_w \) is the density of water. It is reasonable to assume that \( \rho_s/\rho_w = 2.5 \).

\[ \text{FIG. 6. Plot of the normalized diffusivity according to the model by Tokita et al. (1996).} \]

\[ M^{1/3} (w \rho_{bulk}/100)^{1/3} \quad (g^{1/12}/ml^{1/4}) \]

Data points are fitted to equation 4 by a least squares method to obtain \( c = 0.449 \) ml\(^{1/4}\)/g\(^{1/3}\).
The numerical constant, $\beta$ was calculated by the random-covering computer simulations to be 5–9 (Nakashima, 2000a). If $\rho_s/\rho_w = 2.5$, the fit of equation 3 to the data obtained is best for $\beta = 6.2$ (Fig. 5) which falls in the estimated range 5–9. Figure 5 indicates that the fit is good, particularly for $w < 25$ wt.% or $\phi < 12$ vol.%. When $w$ increases to approach the percolation threshold, the randomly scattered obstacles occupy almost all of the three-dimensional space, which makes the diffusivity infinitely small (Trinh et al., 2000). On the other hand, percolation clusters of the pore-space for random walk survive in the real dense gel with high $w$ because the clay mineral packing has an ordered structure such as ‘card-house’ structure (e.g. Yong, 1999). This is a possible reason for the underestimate of $D/D_0$ by equation 3 for $w > 25$ wt.%. Except for the underestimate, however, the fit of equation 3 to the NMR data is good. It suggests that the clay grain distribution in the dilute clay gel whose porosity is as high as 88 vol.% or more is spatially random.

Another diffusion model is applicable to the data of Table 1. Tokita et al. (1996) showed that the normalized diffusivity of small and non-reactive chemical species obeys:

$$D/D_0 = \exp[-cM^{1/3}(wp_{bulk}/100)^{3/4}]$$  \hspace{1cm} (4)

where $c$ is a numerical constant and $M$ is the molecular weight of the random walker (e.g. $M = 18.0$ g for H$_2$O). The chemical interaction (e.g. bound walkers near solid surfaces) is ignored in their model, so that the controlling factor of the diffusivity is the geometry of the random walker and the gel structure. The model by Tokita et al. (1996) is for diffusion in a polymer network with a specific mesh-size or characteristic interval of the cross-linkage. It is possible to apply the model to the clay gel by taking ‘mesh-size’ as ‘pore-size’. The fitting of equation 4 to the diffusion data shows reasonable agreement (Fig. 6). The fitted value of $c$ is 0.449 ml$^{3/4}$/g$^{13/12}$ while $c$ for the poly-acylamide gel is ~0.55 ml$^{3/4}$/g$^{13/12}$ (Tokita et al., 1996). The difference in $c$ is possibly derived from the difference of the detail of the geometrical structure of the pore between the polymer and clay. Except for this difference, however, equation 4 follows the data points of the wide range. Thus Fig. 6 shows that the polymer-network model ignoring the effects of bound H$_2$O is applicable to the water-rich clay gel.

An empirical equation 2 for hectorite gel was found to be applicable also to stevensite gel. The diffusion models by Netz & Dorfmüller (1997) and Tokita et al. (1996) explained the diffusion data successfully. Gels of stevensite or hectorite are characterized by high porosity or high water content which allows the suggestions that: (1) the effects of bound water are negligible; and (2) the solid distribution is spatially random. Thus, the models would also be applicable to water-rich gels of other smectite.

ACKNOWLEDGMENTS

The author thanks anonymous referees for reviewing the manuscript. Free samples of stevensite were provided by Kunimine Industries Co., Ltd. The author is grateful to Yuka Nakashima for help with the NMR experiments and for Mathematica programming of the random covering. This study was supported by a grant from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese government.

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