

Neutron Scattering Study on Dynamics of Water Molecules in MCM-41. 2. Determination of Translational Diffusion Coefficient

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Received: September 2, 2004; In Final Form: February 8, 2005

Quasielastic neutron scattering (QENS) spectra of water-filled MCM-41 samples (pore diameters: 21.4 and 28.4 Å) were measured over the temperature range 238–298 K and the momentum transfer range 0.31–0.99 Å⁻¹ to investigate the dynamics of confined water molecules. The spectra, which consist mainly of contributions from the translational diffusion of water molecules, were analyzed by using the Lorentzian and the stretched exponential functions. Comparison of the fits indicated that the latter analysis is more reliable than the former one. The fraction of immobile water molecules located in the vicinity of the pore walls, which give an elastic component, was found to be 0.044–0.061 in both pores. The stretch exponent β was determined as 0.66–0.80. It was shown that the translational diffusion of water molecules in the pores is decelerated by confinement and that the deceleration becomes marked with a decrease in pore size. The ratios of the translational diffusion coefficient D_T of confined water to that of bulk water at room temperature were within a range of 0.47–0.63.

Introduction

The properties of water confined in a nanospace of mesoporous silica have widely been investigated by using various experimental techniques, such as neutron scattering,^{1–11} NMR,^{2,12–15} XRD,^{16,17} and DSC,^{1,2,18} because these systems can be regarded as a model for various types of interfacial water that play an important role in catalyst, biological membranes, and many other fields. Molecular dynamics (MD) simulations^{19–24} of confined water have also been carried out, and their results were compared with the experimental ones. These investigations have shown that confined water has different structural and dynamic properties from those of bulk water due to both geometrical confinement and interaction with the pore wall. However, it should be pointed out that conventional porous materials, such as Vycor glass and sintered silica, have a rather wide distribution of pore sizes and shapes, which bring in an ambiguity in interpretations of the experimental results. This problem has been solved by preparing MCM-41²⁵ and SBA-15,²⁶ which are mesoporous silica with highly controlled cylindrical channels and a very narrow pore size distribution. So far, the authors have studied the physicochemical properties of water confined in the mesopores of MCM-41 by using quasielastic neutron scattering (QENS)¹ and XRD¹⁶ techniques. The results have shown that water molecules confined in MCM-41 have lower mobility and have a more distorted hydrogen bond network than bulk water.

The previous QENS study¹ was performed by using the spectrometer AGNES²⁷ of the Japan Atomic Energy Research Institute whose neutron wavelength is 4.22 Å. Because the half-width at half-maximum (hwhm) of the resolution function of AGNES is rather large (~ 80 μ eV), we could not determine accurately the translational diffusion coefficient of water molecules. Moreover, since the QENS spectrum is composed of both contributions from the translational and rotational diffusions, we have separated them into two components by an analytical fitting procedure. In the present study, we remeasured QENS spectra of water confined in MCM-41 with the high-resolution spectrometer MIBEMOL²⁸ of LLB by using the 9 Å neutron beam, which consists mainly of contribution from the translational diffusion. The present data enable us to determine more precise values of the translational diffusion coefficient of water molecules in MCM-41. We also investigated the effect of pore size on the translational diffusion coefficient with MCM-41 samples having different pore diameters (21.4 and 28.4 Å).

In the previous QENS study,¹ the spectra were analyzed by a model first employed by Teixeira et al. in their QENS study for bulk water²⁹ and adopted by many researchers.^{3,10} In this model, the contributions of both translational and rotational diffusions of water molecules are considered and the former is expressed by a single Lorentzian function. Recently, this model has been questioned by MD studies of supercooled bulk water^{30–33} and confined water.^{21–23} In these reports, Fourier transform of the stretched exponential function instead of a single Lorentzian function was used to represent the dynamic structure factor of the translational diffusion of water molecules.

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TABLE 1: Pore Diameters and Mole Fraction of Each Component of Physisorbed Water in the C10 and C14 Samples

| sample | pore diameter/ nm | monolayer water | capillary-condensed water |
|--------|----------------------|--------------------|------------------------------|
| C10 | 2.14 | 0.176 | 0.824 |
| C14 | 2.84 | 0.104 | 0.896 |

Some researchers have analyzed their QENS data of water confined in Vycor glass,^{4,5} MCM-41,^{7,8} and MCM-48⁸ by using the stretched exponential function. It is expected that the analysis with a single Lorentzian function is inferior to that with a stretched exponential function, because the former corresponds to a special case of the latter, i.e., the stretched exponent β is equal to unity. In this study, the QENS spectra measured with the spectrometer MIBEMOL are analyzed by using a Lorentzian function and a stretched exponential function, respectively, to investigate the difference of results obtained. This enables us to estimate errors in the results of the past QENS studies in which the former function was used.

Experimental Section

Sample Preparation. Two kinds of MCM-41 samples (C10 and C14) were prepared by the method of Beck et al.²⁵ The MCM-41 samples used in this study were the same as the previous ones.¹ The MCM-41 samples were characterized by electron microscopy, XRD, and N₂ adsorption measurements. Adsorption isotherms of water were measured and the monolayer capacity was estimated with the BET theory. The pore diameters and mole fractions of monolayer water and capillary-condensed water, which is the physisorbed water other than monolayer, are listed in Table 1. Other properties determined (amount of surface hydroxyl groups, isosteric heat of adsorption of water, melting temperature of confined water, etc.) were described in the previous paper.¹

For the neutron scattering measurements, we prepared two “water-filled samples”, i.e., the C10 and C14 samples whose mesopores were filled with water. The details of preparations of the water-filled samples were as follows. The MCM-41 powder was packed into a rectangular aluminum cell 30 × 48 mm² and 0.5 mm sample thickness. The sample cell was set in a vacuum chamber and evacuated for 1 day by using a turbomolecular pump at room temperature and then exposed to water vapor (relative pressure $P/P_0 = 0.7$ – 0.8) for 2 days at room temperature to achieve the capillary condensation of water. Finally, helium gas was introduced in the vacuum chamber to equate the internal pressure to the ambient pressure, and the cell was sealed with indium wire. In addition, we prepared dried MCM-41 samples by the following method. The water-filled sample packed into the cell was set in a vacuum chamber and evacuated for 8 h at room temperature. After the evacuation, helium gas was introduced in the vacuum chamber and the cell was sealed with indium wire. It is noted that the dried samples contain the surface hydroxyls and a trace amount of water molecules adsorbed very strongly on the pore wall.

Neutron Scattering. The QENS spectra were measured by using neutron beams with wavelengths of 9 Å on the spectrometer MIBEMOL (G6–2)²⁸ of LLB, Saclay. The energy resolutions were 14 μ eV (half-width at half-maximum, hwhm). The flat aluminum sample cell was oriented by 135° to the incident neutron beam, and the QENS spectra were measured in a transmission mode. The range of momentum transfer Q was 0.31–0.99 Å^{−1}. In the present study, the spectra at $Q < 0.5$ Å^{−1} were not used because they contain a negligible contribution

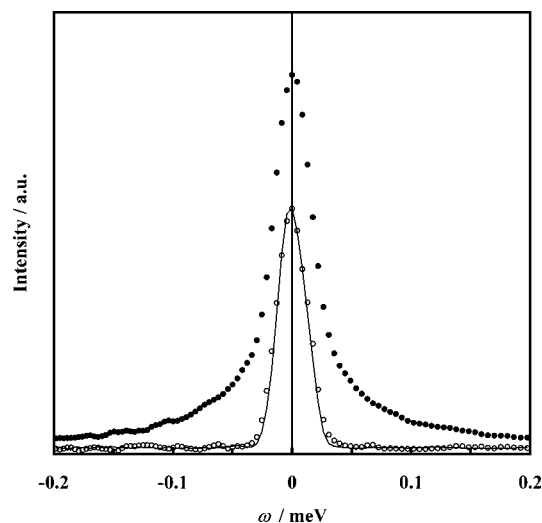


Figure 1. The quasielastic neutron scattering (QENS) spectra of the water-filled (closed circles) and dried (open circles) C10 samples at $T = 298$ K and $Q = 0.85$ Å^{−1}. The solid line represents the spectrum of the vanadium plate (the resolution function of the spectrometer).

from the coherent scattering due to the periodic structure of MCM-41. The temperature range measured was 238–298 K in which water confined in the C10 and C14 samples maintains the liquid state.¹ The sample temperature was controlled within ± 0.2 K by circulating a liquid medium in a sample holder with a temperature-controlling unit. The resolution function of the spectrometer was determined with a vanadium plate. The transmission factors of all the samples were larger than 95%.

Methods of Analysis of QENS Spectra

QENS spectra of the water-filled samples consist of contributions from confined water, surface hydroxyls, MCM-41, and the sample cell. Those of the dried samples, on the other hand, consist of contributions from the last three. Figure 1 shows examples of QENS spectra of the water-filled and dried samples (C10 sample at $T = 298$ K and $Q = 0.85$ Å^{−1}). The shape of the spectrum of the dried sample coincides with that of the vanadium plate, i.e., it is purely elastic. It indicates that not only the surface hydroxyls but also the remaining water molecules, if they exist, are fixed on the pore wall. To derive net spectra of confined water, the spectra of dried samples were subtracted from those of the water-filled samples in advance of the analysis. It can be regarded that the QENS spectra of confined water contain a contribution only of incoherent scattering from hydrogen atoms because of their extremely large incoherent scattering cross section.

Molecular dynamic simulation²² for water confined in Vycor glass has shown that motion of water molecules near the pore wall is much slower than that of the water molecules in the inner part of the pores. In the previous study,¹ the QENS measurement of a MCM-41 sample having only monolayer water has shown that translational motion of the monolayer water molecules is strongly depressed. A similar result was obtained by QENS measurement³ for partially hydrated Vycor glass. These results imply that part of water molecules are strongly adsorbed on the pore wall, which is probably caused by hydrogen bonds between the water molecules and the surface hydroxyls, and motion of these molecules is much slower than that of other molecules. Then, we write the dynamic structure factor $S(Q, \omega)$ of confined water as follows,

$$S(Q, \omega) = CS_{\text{slow}}(Q, \omega) + (1 - C)S_{\text{fast}}(Q, \omega) \quad (1)$$

where $S_{\text{slow}}(Q, \omega)$ and $S_{\text{fast}}(Q, \omega)$ correspond to contributions from the slow molecules near the pore wall and from the other fast ones, respectively. C is the ratio of the slow molecules to the total confined molecules and a Q -independent constant.

In the quasielastic region, the dynamic structure factor of water can be written by a convolution of those of vibrational, translational, and rotational motions.^{29,34,35} Then, $S_{\text{fast}}(Q, \omega)$ is given by

$$S_{\text{fast}}(Q, \omega) = S_V(Q, \omega) \otimes S_T(Q, \omega) \otimes S_R(Q, \omega) \quad (2)$$

Here, \otimes signifies a convolution in ω . $S_V(Q, \omega)$, $S_T(Q, \omega)$, and $S_R(Q, \omega)$ are the dynamic structure factors of vibrational, translational, and rotational motions of the fast water molecules, respectively. $S_V(Q, \omega)$ is expressed by

$$S_V(Q, \omega) = A(Q)\delta(\omega) + B(Q) \quad (3)$$

where $\delta(\omega)$ represents a δ -function. $A(Q)$ is the Debye–Waller factor (DWF) and is given by

$$A(Q) = \exp(-Q^2\langle u^2 \rangle/3) \quad (4)$$

where $\langle u^2 \rangle$ is the mean-square vibrational amplitude of hydrogen atoms. According to the mode-coupling theory of supercooled liquid,^{36–38} $A(Q)$ can be interpreted as the elastic incoherent structural factor (EISF) of a cage around a molecule that is composed of its neighbor molecules and traps it transiently until the structural relaxation occurs. In this interpretation, $\langle u^2 \rangle^{1/2}$ corresponds to a radius of the cage. $B(Q)$ is the ω -independent background due to the vibrational motion. Strictly speaking, $S_T(Q, \omega)$ contains an elastic component whose intensity is EISF of the mesopores of MCM-41.^{3,34} However, in the spherical pores, the elastic component can be neglected at $QR > 4$,^{3,34} where R and Q represent the pore radius and the momentum transfer, respectively. In the case of long cylindrical pores, as in the present case, it disappears at much smaller QR .³⁴ In the present study, the elastic component is negligible since the condition $QR > 4$ is satisfied ($R = 10.7\text{--}14.2 \text{ \AA}$, $Q = 0.56\text{--}0.99 \text{ \AA}^{-1}$). $S_R(Q, \omega)$ is written by the well-known Sears formalism,³⁹

$$S_R(Q, \omega) = j_0^2(Qa)\delta(\omega) + 3j_1^2(Qa)L\left(\omega, \frac{1}{3\tau_R}\right) + \dots \quad (5)$$

where $L(\omega, \Gamma)$ is a Lorentzian function with a half-width at half-maximum (hwhm) of Γ . $j_l(x)$ are spherical Bessel functions. a stands for the radius of rotation (0.98 \AA , the O–H distance of the water molecule). τ_R denotes a relaxation time of rotational diffusion. In the present experimental Q range, the first term is the principal one. For simplicity, we used only a δ -function to represent $S_R(Q, \omega)$, i.e.,

$$S_R(Q, \omega) = \delta(\omega) \quad (6)$$

According to eqs 2–4 and 6, $S_{\text{fast}}(Q, \omega)$ is given by

$$S_{\text{fast}}(Q, \omega) = \exp(-Q^2\langle u^2 \rangle/3)S_T(Q, \omega) + B(Q) \quad (7)$$

$S_{\text{slow}}(Q, \omega)$ is also written by a convolution of dynamic structure factors of vibrational, translational, and rotational motions and each factor can be expressed by the same manner as $S_{\text{fast}}(Q, \omega)$. In this study, we assume that DWF of the slow molecules is the same as that of the fast molecules to reduce the number of fitting parameters. In the previous QENS study,¹ spectra of a MCM-41 sample having only monolayer water

could be reproduced by a model in which the dynamic structure factor of translational motion is represented by a δ -function. Therefore, we assume that, for translational motion, the slow water molecules are immobile on the experimental time scale, and the dynamic structure factor of translational motion is represented by a δ -function. The dynamic structure factor of rotational motion is also represented by a δ -function, which is the same assumption as the case of the fast water molecules.

According to the above discussions, we write the dynamic structure factor of total confined water $S(Q, \omega)$ as follows,

$$S(Q, \omega) = \exp(-Q^2\langle u^2 \rangle/3)[C\delta(\omega) + (1 - C)S_T(Q, \omega)] + B(Q) \quad (8)$$

In this study, we analyzed the QENS spectra by the following three methods which have been used in the past QENS studies on confined water and are different from each other in treatments of $S_T(Q, \omega)$ and the fraction of elastic component C in eq 8.

Method A (Method with δ and Lorentzian Functions). In many QENS studies on the dynamics of water molecules,^{1,3,10,29} $S_T(Q, \omega)$ has been represented by a single Lorentzian function $L(\omega, \Gamma_T)$, i.e.,

$$S_T(Q, \omega) = L(\omega, \Gamma_T) \quad (9)$$

where Γ_T represents a half-width at half-maximum (hwhm) for the translational diffusion. The analysis with eqs 8 and 9 is named “Method A”. Method A is essentially equivalent to “Model 1” in the previous study,¹ except for the following two points: (1) Raw QENS spectra of water-filled samples without subtraction of those of dried sample were used in the previous study. As a result, the elastic component contains contributions from MCM-41 and surface hydroxyls. (2) $S_R(Q, \omega)$ was disregarded in Method A.

Method B (Method with δ and Stretched Exponential Functions). Recently, Chen et al. have proposed use of the Fourier transform of the stretched exponential function (eq 10), instead of eq 9, to represent $S_T(Q, \omega)$ of water molecules on the basis of their MD studies.^{21–23,30–33} According to the notation of the present paper, this model function is given by

$$S_T(Q, \omega) = \frac{1}{\pi} \int_0^\infty dt \cos(\omega t) \exp\left[-\left(\frac{t}{\tau_s}\right)^\beta\right] \quad (10)$$

Actually, Chen et al. have proposed a model function in which $S_T(Q, \omega)$ is given by the right-hand side of eq 10 multiplied by $A(Q)$. However, their $S_T(Q, \omega)$ contains $S_V(Q, \omega)$, which causes $A(Q)$. In the notation of this paper, $S_T(Q, \omega)$ does not contain $S_V(Q, \omega)$, so that $A(Q)$ disappears from eq 10. In eq 10, β is the stretch exponent and represents nonexponentiality of the relaxation function, i.e., the intermediate scattering function in the present case. When $\beta = 1$, eq 10 is reduced to eq 9. τ_s is a characteristic time of the stretched exponential function. In general, values of β and τ_s depend on the momentum transfer Q . Historically, the stretched exponential function, which is also called the Kohlrausch–Williams–Watts (KWW) function, was first proposed as an empirical one.⁴⁰ This function has been interpreted as a result of distribution of relaxation times, i.e., a linear combination of exponential functions with different relaxation times.⁴¹ According to this interpretation, β represents an extent of distribution of relaxation times, and the average relaxation time τ_{av} is given by

$$\tau_{\text{av}} = \int_0^\infty dt \exp\left[-\left(\frac{t}{\tau_s}\right)^\beta\right] = \frac{\tau_s}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (11)$$

The stretched exponential function is predicted by, e.g., the mode-coupling theory for the liquid state,^{36–38} and distribution of relaxation times intrinsically exists in any liquid state. For confined liquid, relaxation times of water molecules in the inner part of the pore must have another distribution due to the effect of the slow water molecules near the pore wall, i.e., the molecular motion will gradually become slower as the distance from the pore wall decreases. In the present system, the both contributions of distribution of relaxation time are represented by eq 10. The analysis using eqs 8, 10, and 11 is named “Method B”. Note that $S(Q, \omega)$ in Method B contains the elastic component (δ -function). A similar method was used in the QENS studies on water confined in MCM-41^{7,8} and MCM-48.⁸ In these studies, however, raw QENS spectra of water-filled samples without subtraction of those of the dried sample were used. In addition, the DWF is multiplied only for the quasielastic component, while the DWF is multiplied for both elastic and quasielastic ones in the present study (see eq 8).

Method C (Method with only Stretched Exponential Function). In eq 8, the contribution from the slow water molecules was expressed by a δ -function. However, the existence of the slow water molecules can also be regarded as a part of the distribution of mobility in confined water. According to this point of view, $[C\delta(\omega) + (1 - C)S_T(Q, \omega)]$ in eq 8 is expressed by a Fourier transform of the stretched exponential function. This corresponds to analysis using eqs 8, 10, and 11 with setting C in eq 8 to be zero. This analysis is named “Method C”, in which there is no elastic component. Zanotti et al. adopted the same method in the analysis of their QENS spectra of water in Vycor glass.⁴

Details of Least-Squares Refinement of QENS Spectra. The spectra of confined water were analyzed by a least-squares refinement procedure with a program KIWI,⁴² in which experimental data were fitted with $S(Q, \omega)$ convoluted with the resolution function of the instrument. Five spectra measured at different Q values were fitted simultaneously. In this fitting procedure, values of the fitting parameters $\langle u^2 \rangle$ and C in eq 8 are common to all the spectra. Values of the other fitting parameters were determined for each spectrum. The fitting parameters finally obtained depended on their starting values, and every result gave almost the same standard deviation. This is because the present least-squares fitting has many variables to determine (13–18 variables) and a large nonlinearity. Accordingly, we estimated the uncertainty of each parameter value by fitting with various initial values of each parameter. As the temperature goes down, the line width of the quasielastic component becomes narrower, which makes it difficult to distinguish between elastic and quasielastic components, i.e., to determine values of C (the fraction of elastic component). Thus, C values for C10 and C14 samples were determined from the spectra at 298 K (highest temperature), which have the largest line width. Then, it was assumed that the C values do not change with temperature. This is not so unrealistic because the number of water molecules adsorbed strongly on the pore wall, which is mainly determined by the number of adsorption sites (surface hydroxyls), will not change largely with temperature. In addition, it should be pointed out that water confined in the C10 and C14 samples does not freeze in the temperature range measured in this study.¹ If the confined water freezes, C values would change at the freezing point.

Results and Discussion

Examples of the fitting results for QENS spectra of the confined water (C14 sample at 298 K) with Methods A, B, and

TABLE 2: Parameters Determined by Method A (method with δ and Lorentzian functions)

| sample | T/K | C | $\langle u^2 \rangle^{1/2}/\text{\AA}$ | $D_T/10^{-10} \text{ m}^2 \text{ s}^{-1}$ | τ_0/ps |
|--------|-------|-------------------|--|---|--------------------|
| C10 | 298 | 0.084 ± 0.009 | 0.51 ± 0.06 | 12.0 ± 0.3 | 2.0 |
| | 283 | | 0.46 ± 0.11 | 6.8 ± 0.2 | 12.1 |
| C14 | 298 | 0.096 ± 0.004 | 0.48 ± 0.11 | 18.3 ± 1.1 | 3.4 |
| | 268 | | 0.44 ± 0.04 | 6.9 ± 0.5 | 7.0 |
| bulk | 298 | — | 0.48^a | 23.0^b | 1.10^b |

^a The literature values of bulk water in ref 29 (253–293 K). ^b The literature values of bulk water in ref 3.

TABLE 3: Parameters Determined by Method B (method with δ and stretched exponential functions)

| sample | T/K | C | $\langle u^2 \rangle^{1/2}/\text{\AA}$ | β_{av} | $D_T/10^{-10} \text{ m}^2 \text{ s}^{-1}$ |
|--------|-------|-------------------|--|-----------------|---|
| C10 | 298 | 0.044 ± 0.006 | 0.44 ± 0.15 | 0.78 ± 0.04 | 10.7 ± 0.1 |
| | 283 | | 0.32 ± 0.12 | 0.80 ± 0.09 | 4.8 ± 0.1 |
| C14 | 298 | 0.061 ± 0.008 | 0.45 ± 0.15 | 0.76 ± 0.04 | 14.5 ± 0.4 |
| | 268 | | 0.25 ± 0.05 | 0.66 ± 0.05 | 4.7 ± 0.1 |

TABLE 4: Parameters Determined by Method C (method with only stretched exponential function)

| sample | T/K | $\langle u^2 \rangle^{1/2}/\text{\AA}$ | β_{av} | $D_T/10^{-10} \text{ m}^2 \text{ s}^{-1}$ |
|--------|-------|--|-----------------|---|
| C10 | 298 | 0.15 ± 0.12 | 0.70 ± 0.04 | 9.1 ± 0.1 |
| | 283 | 0.27 ± 0.06 | 0.78 ± 0.08 | 4.1 ± 0.1 |
| C14 | 298 | 0.34 ± 0.12 | 0.62 ± 0.06 | 12.8 ± 0.2 |
| | 268 | 0.12 ± 0.02 | 0.63 ± 0.03 | 3.7 ± 0.1 |

C are shown in Figure 2. The spectra were fitted almost equally well with the three methods. The reason is that the experimental QENS spectra are broadened due to the resolution function of the instrument. Zanotti et al. reported a similar result for their analysis of water confined in Vycor glass.⁴ To compare the accuracy of the fits, fitted curves for a QENS spectrum (C14 sample, $T = 298 \text{ K}$, $Q = 0.85 \text{ \AA}^{-1}$) obtained by Methods A, B, and C are plotted together in Figure 3. In general, least-squares fitting is improved as the number of parameters allowed to vary is increased. The number of independent variables used in Methods A, B, and C was 13, 18, and 17, respectively. As shown in Figure 3, fitting with Method B reproduced the experimental data best, which is the expected result since Method B has the maximum number of independent variables. Although Method B will give the most reliable values concerning the dynamics of the water molecules, we did perform the analyses with Methods A and C as well, which were adopted in the past QENS study on confined water, to investigate the method dependence of the values. Examples of the temperature dependence of the QENS spectra (C14 sample at $Q = 0.85 \text{ \AA}^{-1}$) are shown in Figure 4. The lower the temperature, the narrower the line width, which indicates slowing down of the motion of water molecules. The spectra at the lowest temperatures (C10 sample, 261 K; C14 sample, 238 K) have too narrow quasielastic wings to be analyzed. This fact will be demonstrated quantitatively later.

By using Methods A, B, and C, values of the fraction of elastic component C , the root-mean-square vibrational amplitude of protons $\langle u^2 \rangle^{1/2}$, the hwhm for the translational diffusion Γ_T (for Method A), the characteristic time of the stretched exponential function τ_s (for Methods B and C), and the stretch exponent β (for Methods B and C) were determined. The results of Q -independent parameters, i.e., C and $\langle u^2 \rangle^{1/2}$, are given in Tables 2–4 with their errors. C corresponds to the fraction of immobile water molecules which are located in the vicinity of the pore wall. According to the C values which are determined by Method B and close to zero (C10, 0.045; C14, 0.061), almost all the confined water molecules are mobile on the experimental time scale. These values are smaller than the fraction of

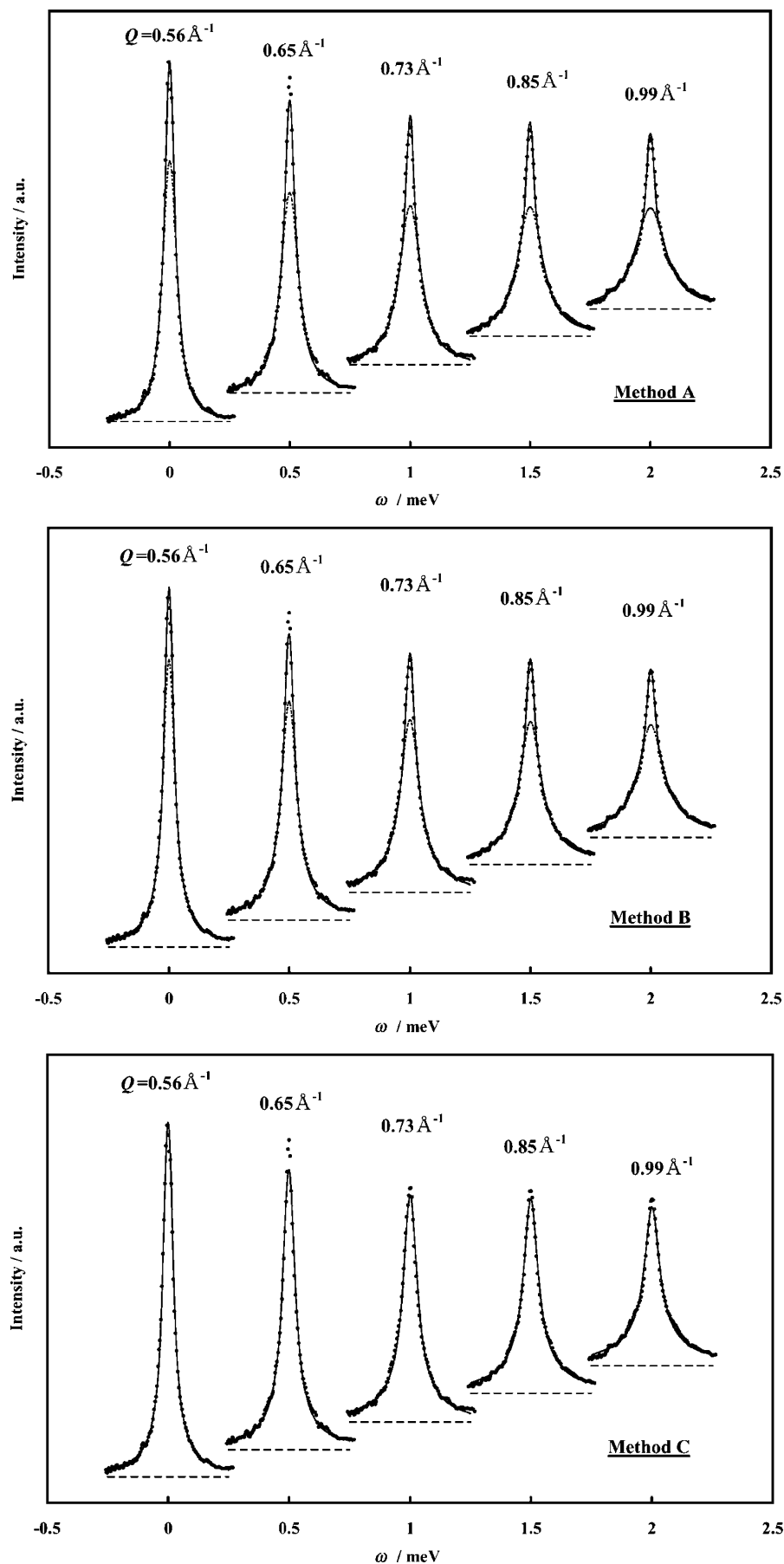


Figure 2. Fitting results for QENS spectra of water confined in the C14 sample at 298 K by using Methods A (upper), B (middle), and C (lower). Closed circles indicate the experimental data. Solid, dotted, and broken lines are for the total fit, the quasielastic component, and the background, respectively.

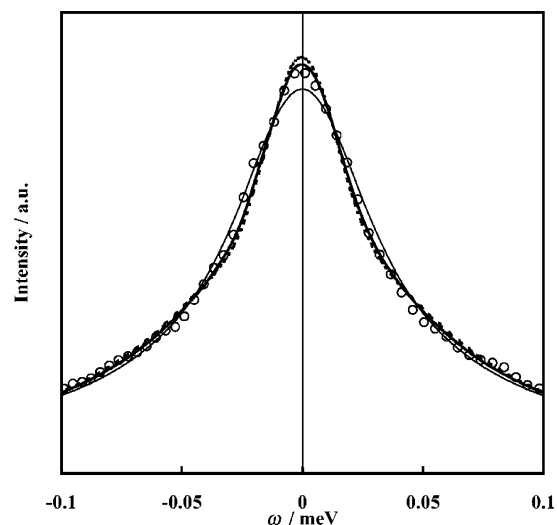


Figure 3. Comparison of fitted curves for a QENS spectrum of water confined in the C14 sample at $T = 298$ K and $Q = 0.85$ Å⁻¹ determined by Methods A (dotted line), B (bold line), and C (fine line). Open circles indicate the experimental data.

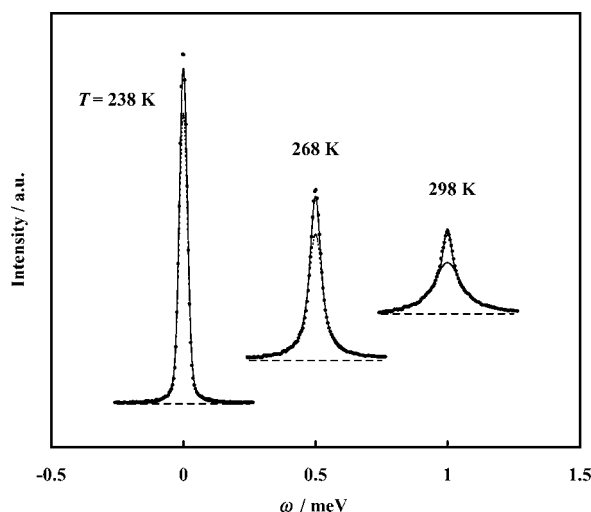


Figure 4. Temperature dependence of QENS spectra of water confined in the C14 sample at $Q = 0.85$ Å⁻¹. Closed circles indicate the experimental data. Solid, dotted, and broken lines are for the total fit, the quasielastic component, and the background determined by Method A, respectively.

monolayer water molecules shown in Table 1 (C10, 0.176; C14, 0.104). This means that part of monolayer water molecules (C10, 26%; C14, 59%) are immobile on the experimental time scale. C values determined by Method A (C10, 0.084; C14, 0.096) are larger than those determined by Method B, which is caused by the fact that, in the analysis with Method A, molecules which are mobile on the experimental time scale but have relatively low mobility are regarded as immobile molecules. It is noted that C values determined by Method A are still smaller than the fraction of monolayer water molecules; 48% (C10) and 92% (C14) of the monolayer molecules are immobile. In the analysis with Method C, C values are fixed to be zero. Methods A and C correspond to extreme cases for the separation of the elastic and quasielastic components which can be performed arbitrarily to a certain extent. It is expected that a real C value exists between the values obtained by Methods A and C. $\langle u^2 \rangle^{1/2}$ corresponds to the vibrational amplitude of water molecules or the radius of the cage trapping a water molecule. The values obtained by Method A are 0.44–0.51 Å, which are similar to the bulk values determined by QENS (0.48 Å)²⁹ and MD (0.4–

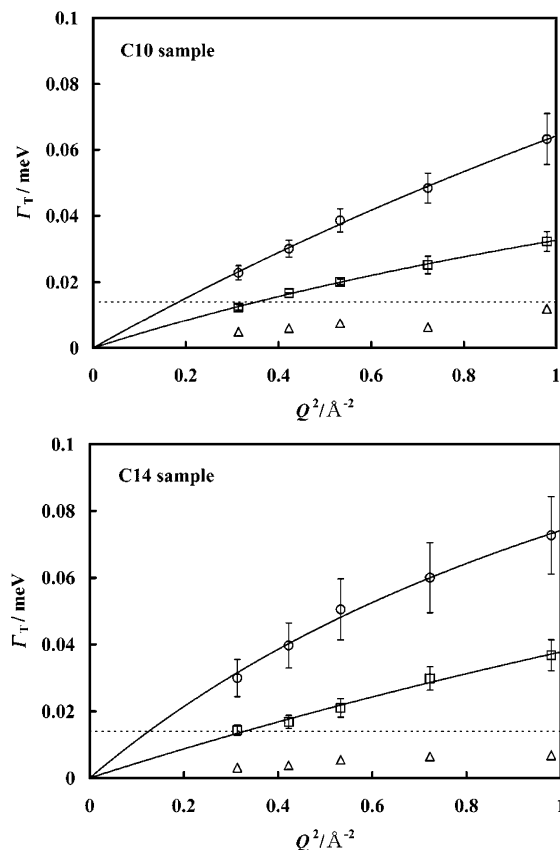


Figure 5. Q^2 dependence of hwhm for the translational diffusion Γ_T obtained by Method A. For the C10 sample (upper), circles, squares, and triangles represent the data at 298, 283, and 261 K, respectively. For the C14 sample (lower), circles, squares, and triangles represent the data at 298, 268, and 238 K, respectively. Vertical lines represent the error bars. Solid lines are fitting results by use of the random-jump-diffusion model (eq 12). The dotted line indicates hwhm of the resolution function of the spectrometer.

0.5 Å),^{31,32} while those obtained by Methods B and C (0.12–0.45 Å) are smaller than the literature ones for bulk water. As seen Table 4, $\langle u^2 \rangle^{1/2}$ values obtained for sample C10 by Method C diminish when the temperature increases, which is unreasonable. This means the approximation used in Method C is not appropriate.

Figure 5 shows the Q^2 dependence of Γ_T obtained by Method A. The Γ_T values at the lowest temperatures (C10 sample, 261 K; C14 sample, 238 K) are smaller than the hwhm of the resolution function (14 μ eV, dotted line in Figure 5), which means that they are not reliable. Therefore, further analysis was not made for the spectra obtained at the lowest temperature. According to a random-jump-diffusion model,⁴³ the Q dependence of Γ_T is given by the equation,

$$\Gamma_T = \frac{D_T Q^2}{1 + D_T \tau_0 Q^2} \quad (12)$$

where D_T and τ_0 are the translational diffusion constant and the residence time of the translational diffusion, respectively. The solid lines in Figure 5 are the results of the fits with eq 12 and reproduce the Γ_T values well. The D_T and τ_0 values determined by the fitting are summarized in Table 2. The D_T values correspond to slopes of the Q^2 – Γ_T plots at $Q \rightarrow 0$ but can be determined approximately in the present Q range (0.56–0.99 Å⁻¹). On the other hand, the τ_0 values determined lack the reliability because they correspond to the inverse of Γ_T

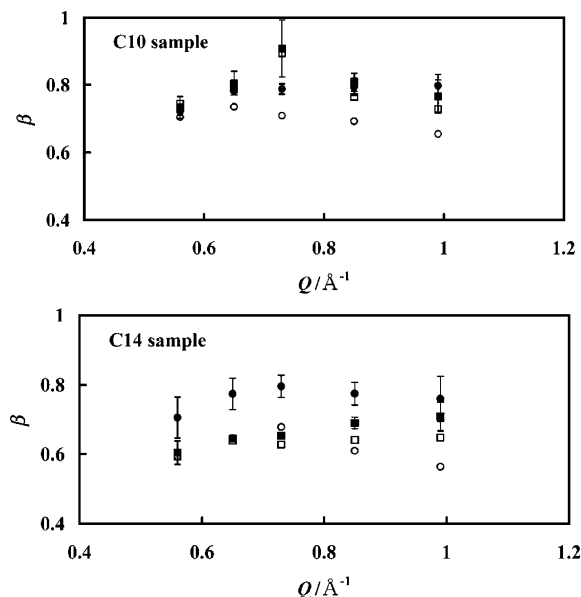


Figure 6. Q dependence of the stretch exponent β obtained by Methods B (closed symbols) and C (open symbols). For the C10 sample (upper), circles and squares represent the data at 298 and 283 K, respectively. For the C14 sample (lower), circles and squares represent the data at 298 and 268 K, respectively. Vertical lines represent the error bars for Method B.

values at $Q \rightarrow \infty$. In general, Γ_T values at $Q > 1 \text{ Å}^{-1}$ are needed to determine reliable τ_0 values. Therefore, the τ_0 values will not be used in the following discussion.

Figure 6 shows the Q dependence of β values determined by Methods B and C. Method A corresponds to a situation in which $\beta = 1$. As shown in this figure, the β values are almost independent of Q and temperature. β values averaged over the measured Q range at each temperature (β_{av}) were calculated and listed in Tables 3 and 4. The β_{av} values determined by Method C are smaller than those determined by Method B. This is reasonable because the elastic component in Method B is regarded as a part of the distribution of mobility in Method C. β_{av} values for the C14 sample are smaller than those for the C10 sample. The reason is probably that the larger pore size of the C14 sample leads to wider distribution of relaxation times since the relaxation time of the confined water molecules will vary with the distance from the pore wall. It is expected that the β_{av} value of water in a much larger pore increases with the pore size because confined water located in the central part of the large pore would have a uniform relaxation time identical with that of bulk water. According to the MD studies on bulk^{31–33} and confined water,²² $\beta = 0.7–1.0$ for the translational diffusion in the Q and temperature range of the present study; β values are not very different from unity. Faraone et al. analyzed their QENS data of water confined in MCM-41 ($d = 25 \text{ Å}$) and MCM-48 ($d = 22 \text{ Å}$) in the temperature range 250–280 K by using the stretched exponential function and determined the β values to be 0.72–0.94.⁸ The present β_{av} values determined by Method B (0.66–0.80) almost coincide with their results. Mansour et al. determined the β values for water confined in MCM-41 ($d = 27 \text{ Å}$) in the temperature range 223–260 K, but their values (0.10–1.05) had a large uncertainty.⁷ Zanotti et al. determined the β values for water confined in Vycor glass ($d = 50 \text{ Å}$) in the temperature range 253–293 K.⁴ In the Q range of the present analysis (0.56–0.99 Å^{-1}), their β values for “100% hydrated sample” range from 0.34 to 0.77 and are significantly smaller than the present results. This must

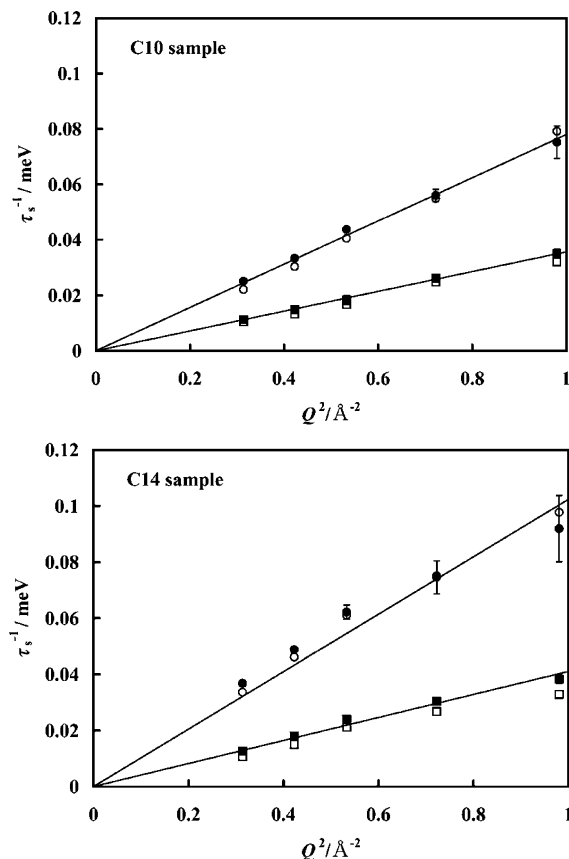


Figure 7. Q^2 dependence of $1/\tau_s$ obtained by Methods B (closed symbols) and C (open symbols). For the C10 sample (upper), circles and squares represent the data at 298 and 283 K, respectively. For the C14 sample (lower), circles and squares represent the data at 298 and 268 K, respectively. Vertical lines represent the error bars for Method B.

be due to a wide distribution of pore size in Vycor glass, which leads to the wide distribution of relaxation time of the confined molecules.

Figure 7 shows the Q^2 dependence of $1/\tau_s$ obtained by Methods B and C. As shown in this figure, $1/\tau_s$ values are almost unchanged with the methods. Figure 8 shows the Q^2 dependence of $1/\tau_{av}$ determined by eq 5. $1/\tau_{av}$ values determined by Method C are smaller than those by Method B. This is due to the fact that the quasielastic component in Method C contains the elastic component in Method B. D_T values of the water molecules should be determined by $1/\tau_{av}$, not by $1/\tau_s$, because the mobility of molecules depends not only on τ_s but also on β . In the analysis of QENS spectra with the stretched exponential function, some researchers adopted the following relation to determine D_T values,^{4,6,8}

$$1/\tau_{av} = D_T Q^\gamma \quad (13)$$

where γ is an exponent. In the present study, the $1/\tau_{av}$ values were fitted by the following equation, because there is a good linear relation between $1/\tau_{av}$ and Q^2 .

$$1/\tau_{av} = D_T Q^2 \quad (14)$$

Equation 14 is equivalent to the hydrodynamic relation, $\Gamma_T = D_T Q^2$. The solid lines in Figure 8 are the fitted ones. The D_T values determined are summarized in Tables 3 and 4. In the present analysis, we neglected contribution to the QENS spectra from the rotational motion of the water molecules (see eqs 6

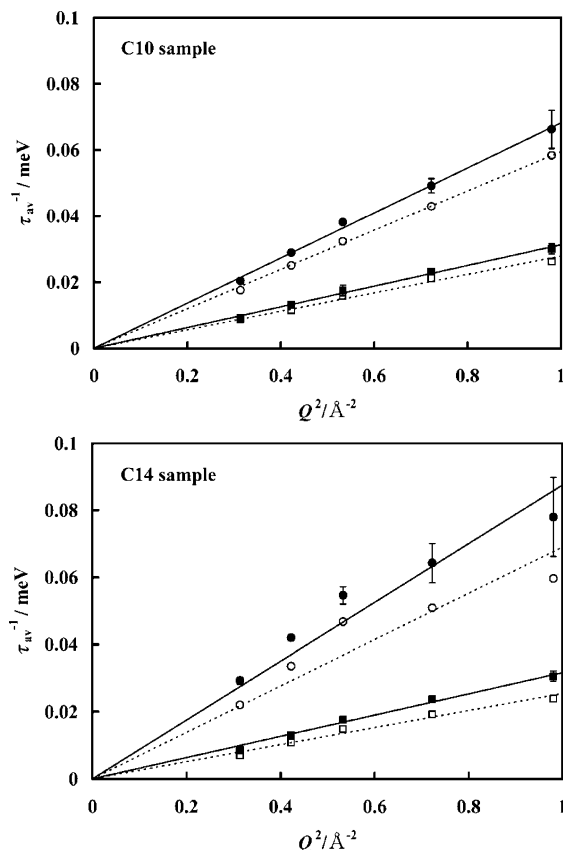


Figure 8. Q^2 dependence of $1/\tau_{av}$ obtained by Methods B (closed symbols) and C (open symbols). For the C10 sample (upper), circles and squares represent the data at 298 and 283 K, respectively. For the C14 sample (lower), circles and squares represent the data at 298 and 268 K, respectively. Vertical lines represent the error bars for Method B. Solid and dotted lines indicate fitting results by use of eq 14 for Methods B and C, respectively.

and 7). This leads to overestimation of the $1/\tau_{av}$ values in the high Q region. However, D_T values will not be affected seriously, because they correspond to slopes of the Q^2-1/τ_{av} plots at $Q \rightarrow 0$, which is mainly determined by the $1/\tau_{av}$ values in the low Q region. For comparison, D_T values were also determined by eq 13. The D_T values almost coincided with those determined by eq 14: the difference was 12% at the maximum. The γ values were 1.7–2.2.

Figure 9 shows an Arrhenius plot of D_T determined by Methods A, B, and C together with the literature values for bulk water²⁹ and for water in MCM-41.¹ The literature values plotted were determined by a method that is equivalent to Method A. For bulk water, it is expected that an analysis with the stretched exponential function would give β values nearly equal to unity and almost the same D_T values, because the QENS spectra of bulk water could be fitted well without the elastic component in the literature.²⁹ In the previous study,¹ D_T values of water in MCM-41 were determined only at 300 K, because the hwhm of the resolution function (80 μ eV) was too large to determine the D_T values at lower temperatures. In the present study, we could determine the D_T values at 268–298 K owing to higher resolution of the spectrometer (14 μ eV). As shown in Figure 9, the three methods give different D_T values from each other; the ratios of D_T values determined with Methods A and C to those with Method B, which are the most reliable values, are 1.12–1.47 and 0.79–0.88, respectively. However, all the results determined by the three methods indicate that the D_T values of the confined water are smaller than those of bulk water and decrease with narrowing of the pore sizes in the whole

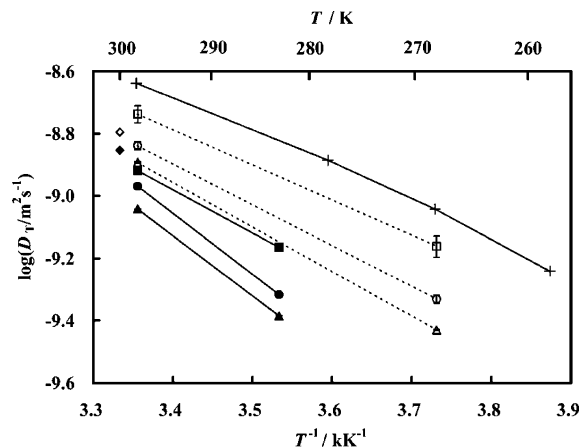


Figure 9. Arrhenius plots of the self-diffusion coefficient of translational diffusion D_T of water molecules in the C10 (closed symbols) and C14 (open symbols) samples determined by using Methods A (squares), B (circles), and C (triangles). Literature values for bulk water²⁹ (+) and the previous results for water in MCM-41¹ (diamonds) are plotted for comparison.

temperature range measured. Therefore, we can conclude that the translational diffusion of the water molecules is decelerated by confinement, which is the same result as that in the previous QENS study.¹ As described above, Methods A and C correspond to extreme cases for the separation of the elastic and quasielastic components, so that a real D_T value exists between the values obtained by Methods A and C.

The ratio of D_T values of confined water to that of bulk water ($D_{T,confined}/D_{T,bulk}$) determined by Method B was 0.47 for the C10 sample (pore diameter $d = 21$ Å) and 0.63 for the C14 sample ($d = 28$ Å) at room temperature. These values are comparable to those reported in other studies at room temperature, i.e., QENS studies on water in Develosil² ($d = 30$ Å, $D_{T,confined}/D_{T,bulk} = 0.61$) and Vycor glass⁴ ($d = 50$ Å, $D_{T,confined}/D_{T,bulk} = 0.55$) and MD studies on water in the cylindrical pore²² ($d = 40$ Å, $D_{T,confined}/D_{T,bulk} \sim 0.5$) and the spherical pore²⁴ ($d = 24$ Å, $D_{T,confined}/D_{T,bulk} = 0.5$ – 0.8). Faraone et al. determined D_T values of water molecules in MCM-41 and MCM-48 at 280 K by QENS study.⁸ Their ratios for MCM-41 ($d = 25$ Å, $D_{T,confined}/D_{T,bulk} = 0.23$) and for MCM-48 ($d = 22$ Å, $D_{T,confined}/D_{T,bulk} = 0.20$) are smaller than the present ones. This may be due to the fact that their ratios were determined at relatively low temperature. As shown in Figure 9, differences between values of $\log D_T$ for bulk and confined water at 280 K become larger than those at 298 K. By using the present result with Method B, the ratio for the C10 sample at 283 K was estimated to be 0.32. Among the literature values of $D_{T,confined}/D_{T,bulk}$, only the values obtained by an NMR study¹² on water in MCM-41 ($d = 18$ – 40 Å, $D_{T,confined}/D_{T,bulk} = 0.0085$ – 0.12) are much smaller than both the present and other literature values shown above.

The XRD study¹⁶ showed that water confined in MCM-41 interacts strongly with the surface hydroxyls and that the hydrogen bond network in confined water is gradually distorted with a decrease in pore sizes. It is expected that the distortion of the hydrogen bond network led to an increase in the mobility of the water molecules. However, the present QENS study confirms the deceleration of translational diffusion of water molecules by confinement. This indicates that the deceleration induced by the interaction with the pore wall and geometrical confinement overcomes the acceleration by the distortion of the hydrogen bond network.

Conclusions

QENS spectra of water confined in MCM-41 samples, which consist of mainly the contribution from the translational diffusion of water molecules, were analyzed by three different methods: Method A (method with δ and Lorentzian functions), Method B (method with δ and stretched exponential functions), and Method C (method with only the stretched exponential function). The results of Method B are most reliable because the experimental data were reproduced best by the fit with Method B. The values of the fraction of elastic component C , which corresponds to the fraction of immobile water molecules located in the vicinity of the pore wall, were estimated by Method B to be 0.045 (C10) and 0.061 (C14). This means 26% (C10) and 59% (C14) of the monolayer molecules are immobile on the experimental time scale. The values of the stretch exponent β were almost independent of Q and temperature. β values averaged over the measured Q range at each temperature (β_{av}) were determined by Method B to be 0.66–0.80, which almost coincided with those in the MD and QENS studies on bulk and confined water. The β values of the C14 sample were smaller than those of the C10 sample. The translational diffusion coefficients of water molecules D_T determined by the three methods were different from each other. However, all the results indicated that the D_T values of the confined water are smaller than those of bulk water and decrease with narrowing of the pore sizes in the whole temperature range measured, which is the same result as the previous QENS study.¹ The XRD study¹⁶ showed that water confined in MCM-41 interacts strongly with the surface hydroxyls and that the hydrogen bond network in confined water is gradually distorted with a decrease in pore sizes. The results of the QENS and XRD studies indicate that the deceleration of diffusion of water molecules induced by the interaction with the pore wall and geometrical confinement overcomes the acceleration by the distortion of the hydrogen bond network. The ratio of D_T of confined water to that of bulk water at room temperature determined by Method B was 0.47–0.63, which is comparable to the literature values in other QENS and MD studies on confined water.

Acknowledgment. This work was partly supported by Grant in Aid for Science Research No. 08454227 from the Ministry of Education, Culture, Sports, Science and Technology of Japan and by a Special Grant for Cooperative Research administered by the Japan Private School Promotion Foundation.

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