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Neutron Scattering Study on Dynamics of Water Molecules Confined in MCM-41

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Abstract. Quasi-elastic neutron scattering (QENS) spectra of water-filled MCM-41 samples having different pore sizes (pore diameters: 2.14 and 2.84 nm) were measured over the temperature range 200–298 K and analyzed by a model in which contributions of translational and rotational diffusions of water molecules are expressed by a linear combination of Lorentzian functions (Teixeira et al., 1985). The results indicated that the translational diffusion is decelerated by confinement and that the deceleration increases with a decrease in pore size. QENS spectra of water-filled MCM-41 samples having the same pore sizes (pore diameter: 3.36 nm) but a different amount of the hydroxyl groups (0.7 and 2.6 OH's/nm^2) were also measured over the temperature range 220–298 K. It was found that the vibrational amplitude of water molecules in MCM-41 increases with increasing amount of the surface hydroxyls, which implies that the hydrogen-bond network of confined water is distorted by interaction with the surface hydroxyls.

Keywords: confined water, MCM-41, surface hydroxyls, quasi-elastic neutron scattering, diffusion coefficient

1. Introduction

The properties of water confined in mesoporous silica have widely been investigated because these systems can be regarded as model systems for various types of interfacial water. Recently, mesoporous materials with very narrow pore size distribution, such as MCM-41, have been developed and used in many experiments in this field. We have studied the properties of water molecules confined in the mesopores of MCM-41 by using QENS (Takahara et al., 1999) and XRD (Smirnov et al., 2000) techniques. The former study was performed by using a spectrometer AGNES of Japan Atomic Energy Research Institute whose neutron wavelength is 4.22 Å and the half-width at half-maximum (HWHM) of the resolution function is rather large (~80 μeV). These studies have shown that water molecules confined

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in MCM-41 have lower mobility and less structured hydrogen-bond network than bulk water, and these tendencies are enhanced with narrowing the pore size.

Recently, we re-measured QENS spectra of water confined in MCM-41 on a high-resolution spectrometer MIBEMOL of LLB to get more precise information about the dynamics of confined water molecules. The measurement was performed by using two different wavelengths (6 and 9 Å) of neutrons; in the former case the translational diffusion of water molecules are mainly concerned, while both of translational and rotational ones are measured in the latter case. The QENS spectra for 9 Å neutron beam have already been analyzed to determine the precise values of the translational diffusion coefficient of water molecules, which will be reported elsewhere (Takahara et al., submitted). The QENS spectra of water have been analyzed by a model in which contributions of translational and rotational diffusions of water molecules are expressed by a linear combination of Lorentzian functions (Teixeira et al., 1985). Recently, some researchers have analyzed their QENS data of confined water by using Fourier transform of the stretched exponential function instead of Lorentzian function (Fraone, 2003; Mansour, 2002; Zanotti, 1999). In our analysis of the QENS spectra for 9 Å neutron beam, the above two models were applied to the same QENS spectra to investigate the difference of results obtained (Takahara et al., submitted). In this paper, we will report the results of analysis using both of the spectra for 6 and 9 Å neutron beams measured on MIBEMOL. This analysis enables us to determine the residence time of translational diffusion of water molecules, which could not be determined precisely by the analysis using only the spectra for 9 Å neutron beam. We will discuss pore-size dependence of the dynamics of confined water molecules.

It is expected that the dynamics of confined water molecules depends not only on pore size but also on the interaction between the pore wall and confined water molecules. The surface hydroxyls on the pore wall must play an important role in this interaction. Therefore, we re-measured QENS spectra of water-filled MCM-41 samples having the same pore sizes but a different amount of the surface hydroxyls on the spectrometer AGNES. In this paper, we will also show the results of this experiment.

2. Experimental Section

Two kinds of MCM-41 samples having different pore diameters d (C10 sample: $d = 2.14$ nm, C14 sample: $d = 2.84$ nm) were prepared by the method of Beck et al. (1992). In addition, MCM-41 samples having the same pore diameter ($d = 3.36$ nm) but a different amount of the hydroxyl groups (C16-A sample: 0.7 OH's/nm^2, C16-B sample: 2.6 OH's/nm^2) were prepared by the method described elsewhere (Mori et al., 2002). The results of characterization of these samples will be given elsewhere (Takahara et al., submitted; Mori et al., in preparation). The MCM-41 samples were evacuated and then exposed to water vapor (relative pressure $p/p_0 = 0.7$–0.8) at 298 K to achieve capillary condensation of water. QENS measurements were carried out by using the spectrometers MIBEMOL (LLB, Saclay) for C10 and C14 samples in the temperature range 200–298 K and AGNES (JAERI, Tokai) for C16-A and C16-B samples in the temperature range 220–298 K.

3. Method of Analysis

The scattering law $S(Q, \omega)$ of the water-filled samples, which consists of contributions from water and MCM-41, can be expressed by the relation

$$\begin{aligned} S(Q,\omega) &= \exp(-Q^2\langle u^2\rangle/3)[C\delta(\omega) \\ &\quad + (1-C)S_{\mathrm{T}}(Q,\omega)\otimes S_{\mathrm{R}}(Q,\omega)] + B(Q). \quad (1) \end{aligned}$$

Here, Q and ω represent momentum and energy transfers, respectively. $\langle u^2\rangle$ is the mean-square vibrational amplitude of water molecules. $\delta(\omega)$ is a δ-function and corresponds to the elastic component. $(1-C)S_{\mathrm{T}}(Q,\omega)\otimes S_{\mathrm{R}}(Q,\omega)$ represents the quasi-elastic component. C is the fraction of the elastic component. $\otimes$ signifies a convolution in ω. $S_{\mathrm{T}}(Q,\omega)$ and $S_{\mathrm{R}}(Q,\omega)$ are contributions from translational and rotational diffusions of the capillary-condensed water molecules, respectively. $B(Q)$ is the ω-independent background due to the vibrational motions. The elastic component in Eq. (1) is ascribable to the contribution of atoms which are immobile on the experimental time scale, e.g., surface hydroxyls and water molecules strongly adsorbed on the pore wall. For $S_{\mathrm{T}}(Q,\omega)$ and $S_{\mathrm{R}}(Q,\omega)$, the following functions (Teixeira et al.,

1985) were used.

$$S_{\mathrm{T}}(Q,\omega) = L(\omega, \Gamma_{\mathrm{T}}), \tag{2}$$

$$S_{\mathrm{R}}(Q,\omega) = j_0^2(Qa)\delta(\omega) + 3j_1^2(Qa)L\left(\omega, \frac{1}{3\tau_{\mathrm{R}}}\right) + 5j_2^2(Qa)L\left(\omega, \frac{1}{\tau_{\mathrm{R}}}\right), \tag{3}$$

where $L(\omega, \Gamma)$ is a Lorentzian function of ω and a half-width at half-maximum (HWHM) Γ. $j_l(x)$ are spherical Bessel functions. a stands for the radius of rotation (0.98 Å, the O-H distance of water molecule). τ_{R} denotes a relaxation time of rotational diffusion. According to a random-jump-diffusion model (Egelstaff, 1967), Q-dependence of Γ_{T} is given by the relation,

$$\Gamma_{\mathrm{T}} = \frac{D_{\mathrm{T}}Q^2}{1 + D_{\mathrm{T}}Q^2\tau_{\mathrm{T}}}, \tag{4}$$

where D_{T} is the translational diffusion coefficient and τ_{T} the residence time of the translational diffusion. The analysis using Eqs. (1)–(4), is the same as “Model 1” in the previous QENS study (Takahara et al., 1999).

The details of least-squares refinement procedure of the QENS spectra are as follows. Fifteen spectra measured at different Q values for 6 and 9 Å neutron beams were fitted simultaneously with Eqs. (1)–(3). The values of the fitting parameters finally obtained depended on their starting values, and each result gave almost the same standard deviation. This is because the present

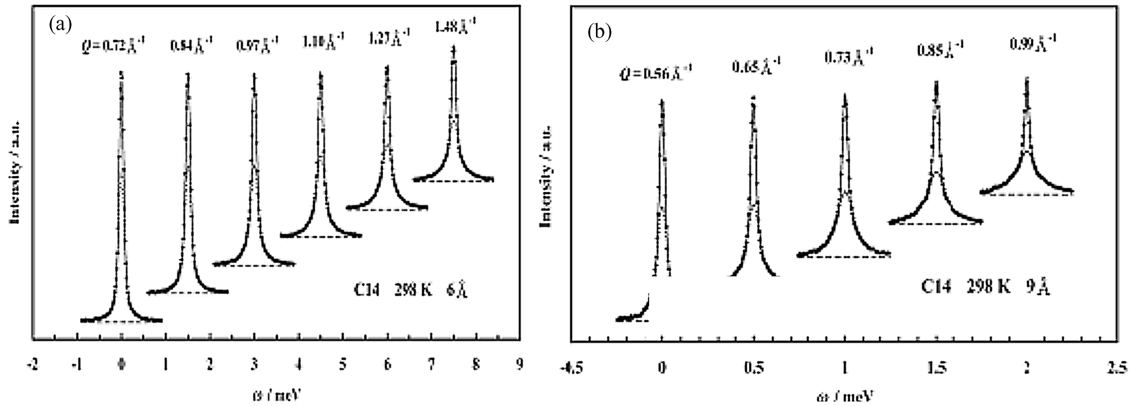

Figure 1. Q-dependence of the quasi-elastic neutron scattering (QENS) spectra for the water-filled C14 sample at 298 K measured with (a) 6 Å and (b) 9 Å wavelength neutrons. Closed circles indicate the experimental data. Solid, dotted and broken lines are for the total fit, the quasi-elastic component and the background, respectively.

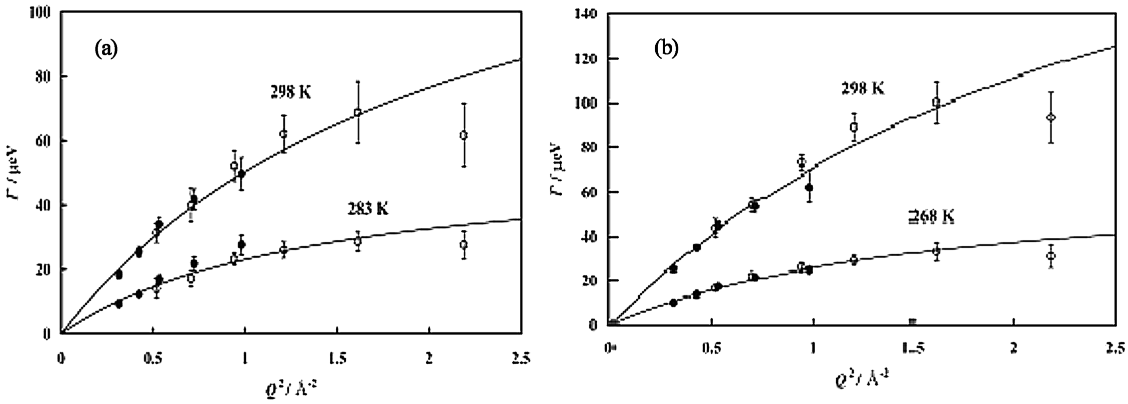

Figure 2. Q-dependence of HWHM for the translational diffusion Γ_{T} of the water-filled (a) C10 and (b) C14 samples determined by the fitting of 9 Å (closed circles) and 6 Å (open circles) spectra. Vertical lines represent the error bars. Solid curves indicate fitting results by use of the random-jump-diffusion model (Eq. 4).

least-squares fitting has many variables (28 parameters) to determine and a large non-linearity. However, we could estimate the uncertainty of each parameter value by fitting with various initial values of each parameter. As the temperature goes down, the linewidth of the quasi-elastic component becomes narrower, which causes ambiguity of fitting. Thus, we assumed that fraction C of elastic component in Eq. (1) does not change with temperature. The spectra other than those at 298 K (highest temperature) were fitted by imposing the C values which had been determined from the spectra at 298 K.

4. Results and Discussion

Examples of the least-squares fitting are shown in Fig. 1, giving successful results. C values obtained were 0.25 for C10 sample and 0.19 for C14 sample, and slightly larger than the ratio of the amount of monolayer water molecules and surface hydroxyls to the total (C10 sample: 0.211, C14 sample: 0.126). This is probably due to the neglect of the distribution of the mobility of confined water molecules (Takahara et al., submitted).

Figure 2 shows the Q-dependence of Γ_T obtained by the fitting. With the spectra obtained at 261 K for C10 sample and 238 K for C14 sample, the analysis was not successful, because their linewidths were smaller than those of the resolution function. The Γ_T values determined for 6 and 9 Å neutron beams almost coincide with each other. Γ_T values for both 6 and 9 Å neutron beams were fitted with Eq. (4). The solid lines in Fig. 2 are the fitting results. It should be pointed out that the τ_T values cannot be determined precisely by using only the 9 Å data because τ_T values correspond to inverse of Γ_T value at $Q \to \infty$.

Figure 3 shows Arrhenius plots of D_T, τ_T and τ_R, together with the literature values for bulk water (Bellissent-Funel et al., 1995) and the previous data (Takahara et al., 1999) for comparison. The D_T values decrease with narrowing of the pore sizes in the whole temperature range measured, indicating that the translational diffusion of water molecules is decelerated by confinement. The present τ_T values almost coincide with the previous ones (Takahara et al., 1999). The τ_T values increase with a decrease in pore sizes, indicating again the deceleration of the translational diffusion by confinement. For the rotational diffusion, we could not obtain reliable information because the present data

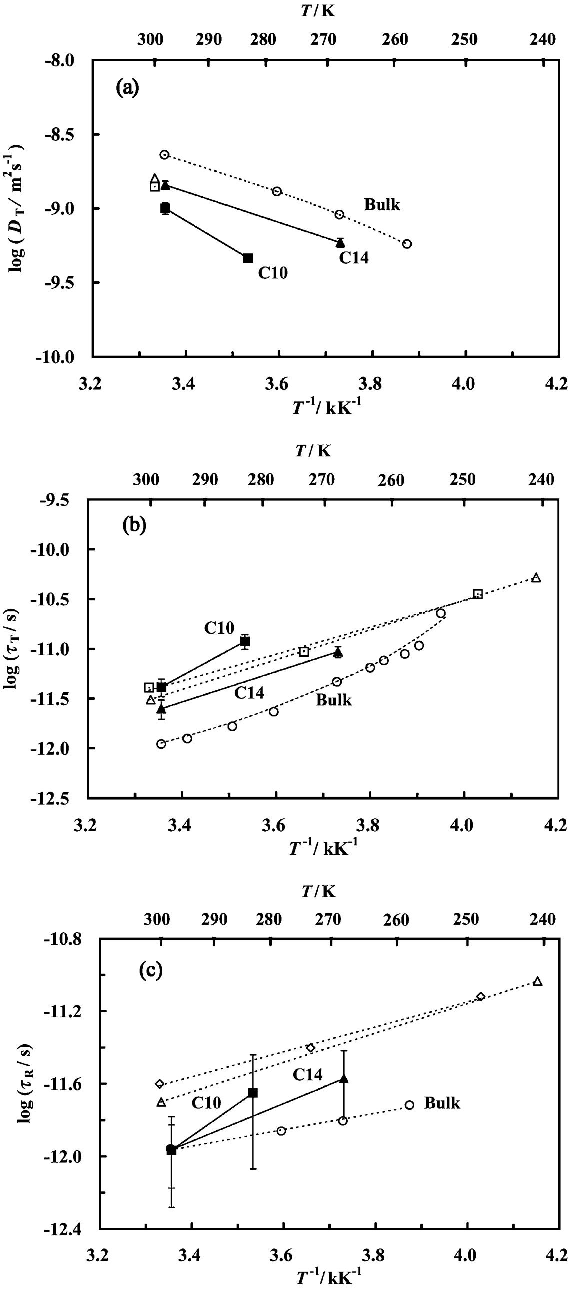

Figure 3. Arrhenius plots of (a) the diffusion coefficient of translational diffusion D_T, (b) the residence time of translational diffusion τ_T and (c) the relaxation time of rotational diffusion τ_R of the capillary-condensed water in C10 (closed squares) and C14 (closed triangles) samples. Literature values for bulk water (open circles; Bellissent-Funel et al., 1995) and the data determined by using "Model 1" in the previous study (open squares: C10 sample, open triangles: C14 sample; Takahara et al., 1999) are plotted for comparison.

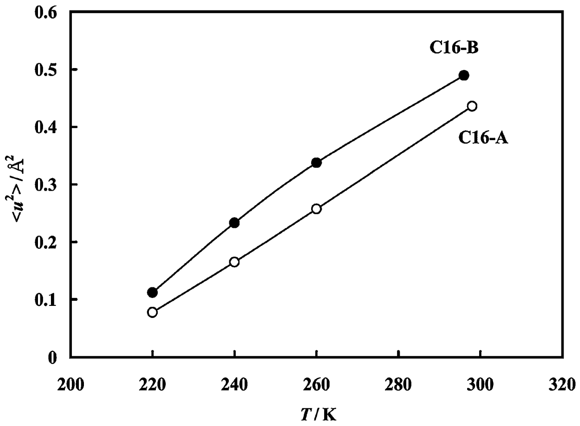

Figure 4. Temperature dependence of the mean-square vibrational amplitude $\langle u^2 \rangle$ of water molecule confined in C16-A (open circles) and C16-B samples (closed circles).

contain large errors as seen by error bars in Fig. 3(c). This is due to the fact that spectra in the Q range measured in this study (0.56–1.48 Å^{-1}) contain rather small contribution of the rotational diffusion. The previous data (Takahara et al., 1999), which were determined in the Q range 0.61–2.38 Å^{-1}, are more reliable for τ_R.

The XRD study (Smirnov et al., 2000) showed that water confined in MCM-41 interact 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 hydrogen-bond network lead 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 hydrogen-bond network.

Figure 4 shows the temperature dependence of the mean-square vibrational amplitude $\langle u^2 \rangle$ of water molecule confined in C16-A and C16-B samples. $\langle u^2 \rangle$ values were determined by Q-dependence of peak intensity of the QENS spectra measured on AGNES. It was found that the vibrational amplitude of water molecules in MCM-41 increases with increasing amount of surface hydroxyls, which implies that the hydrogen-bond network of confined water is distorted by interaction with surface hydroxyls. Entire results obtained by this measurement will be given elsewhere (Mori et al., in preparation).

Acknowledgments

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