

# Quasielastic neutron scattering investigation of motion of water molecules in *n*-propyl alcohol-water mixture

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The dynamics of water molecules in the *n*-propyl alcohol-water mixtures is investigated by using quasielastic neutron scattering measurements. The dynamic structure factor  $S(Q, E)$  obtained from incoherent scattering of hydrogen atoms of water is fitted with jump diffusion and relaxing cage models. The diffusion constant obtained from the relaxing cage model, which gives better fitting with  $S(Q, E)$ , shows better agreement to the experimental value than that of jump diffusion model. The dependence of translational relaxation time  $\tau_T(Q)$  and stretched exponent  $\beta_T(Q)$  on the fraction of hydrophobic hydrating water molecules in the solution is discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073881]

## I. INTRODUCTION

Water is an ubiquitous material on earth, which plays important roles in many fields such as maintaining life. The many functions of water relate to so called “hydration.” A lot of matter can be dissolved in water. Usually water molecules hydrate to ions or polar molecules by electrostatic attraction in aqueous solution. In the aqueous solution of nonpolar molecules, on the other hand, there exists no electric attraction between water and solute. However, it is known that water molecules hydrate even to nonpolar molecules. This kind of hydration is called the “hydrophobic hydration.” Hydrophobic hydration occurs when water molecules form hydrogen bond network around nonpolar solutes. For example, it is known that water molecules correlate with protein molecules or clusters in the cell. Hydrophobic hydration plays an important role in protein folding, protein-protein interactions, formation of lipid bilayer membranes, nucleic acid structures, and protein-small molecule, which closely relate to the function of protein.

In order to examine the role of hydrophobic hydration in nonelectrolyte aqueous solutions, we have specifically paid attention to the dynamical behavior of *n*-propyl alcohol-water mixture.<sup>1-3</sup> Because *n*-propyl alcohol is one of the simplest molecule having nonpolar parts, we believe that understanding the dynamics of water molecules in this solution will be essential knowledge for various application of biological science. The structure of alcohol aqueous solutions were investigated by many researchers.<sup>4-9</sup> Especially, the hydrophobic hydration and the dynamics were analyzed.<sup>10-13</sup> Sato *et al.* measured the dielectric relaxation of 1-propanol-water mixtures and analyzed the thermodynamic quantities and hydrating structure.<sup>14</sup> In order to obtain the information of the concentration fluctuation, small angle neutron scatter-

ing measurements of *n*-propyl alcohol-water mixture at 25 °C have been carried out, using the small/wide angle neutron diffractometer SWAN at the pulsed neutron source KENS of High Energy Accelerator Research Organization (KEK), Japan. The scattering intensities have been analyzed by the large scale reverse Monte Carlo method.<sup>1</sup> As a result, it was observed that *n*-propyl alcohol molecules formed clusters, the shape of which is characterized by mass fractal. These clusters are surrounded by water molecules. The molecules can be divided into two parts. The molecules of one part locate the boundary of the *n*-propyl alcohol clusters (first coordination shell) and are called as “hydrophobic hydrating water.” The other molecules exist away from the alcohol clusters, which are in the bulk state. Moreover it is found that at the *n*-propyl alcohol mole fraction,  $x_p=0.167$ , almost all water molecules are located at the boundary of alcohol clusters,<sup>1</sup> that is, hydrophobic hydration is saturated at this concentration. We have measured quasielastic neutron scattering (QENS) spectra on *n*-propyl alcohol-water mixture and analyzed the excess molar volume of *n*-propyl alcohol-water mixture by using this assumption.<sup>3</sup> Although this approximation was too simple and rough, the validity of it was confirmed by the good agreement of the concentration dependence of the calculated excess molar volume with that of the experiment data.<sup>15</sup>

The diffusional properties of water molecules at the each state are also of important interest. In this present paper, we analyze the QENS spectra for pure water and *n*-propyl alcohol-water mixture by jump diffusion<sup>16</sup> and relaxing cage<sup>17,18</sup> models, then discuss the physical picture of diffusional motion of water molecules in *n*-propyl alcohol-water mixture.

## II. EXPERIMENTAL

The samples were mixtures of *n*-propyl alcohol partially substituted with deuterium, C<sub>3</sub>D<sub>7</sub>OH (ISOTEC, 99.3%D),

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TABLE I. The fraction of hydrophobic hydration water molecules,  $\alpha$ , for the *n*-propyl alcohol aqueous solution of the composition  $x_p$  derived by the procedure of our previous paper (Ref. 3).

$x_p$	$\alpha$
0.0	0.0
0.02	0.30
0.04	0.52
0.06	0.70
0.10	0.87
0.167	1.0

and pure light water, H<sub>2</sub>O. The mole fraction of *n*-propyl alcohol,  $x_p$ , of the sample solutions ranged from 0.0 to 0.167. The fraction of hydrophobic hydrating water molecules,  $\alpha$ , which was derived by the method described in Ref. 3, is listed in Table I for each  $x_p$ . Each mixture was placed in an aluminum cell composed of coaxial double cylinders with the spacing of 0.3 mm between the two and the inner diameter of the outer cylinder of 14.0 mm, that is, the shape of the sample is a thin cylinder of 0.3 mm in thickness and 14.0 mm in outer diameter. The cell was sealed with indium metal.

QENS measurements of *n*-propyl alcohol-water mixture at 25 °C had been carried out using the high-resolution pulse cold neutron spectrometer AGNES of the Institute for Solid State Physics, University of Tokyo. This spectrometer is installed at C3-1-1 beam port of the JRR-3M reactor at Japan Atomic Energy Agency. The incident neutron wavelength was 4.22 Å. The neutron flux at the sample position was  $2.3 \times 10^3$  n/cm<sup>2</sup> s. The range of momentum transfer  $Q$  covered by AGNES spectrometer was from 0.376 to 2.64 Å<sup>-1</sup> with an energy resolution (full width at half maximum) of  $\Delta E = 120$  μeV. The data collection time was 4 h for each run. The time of flight data of scattered neutrons was obtained by 120 <sup>3</sup>He detectors, which are divided into ten blocks of 10° interval. More detail description of experiment is found in our previous paper.<sup>3</sup>

Corrections for attenuation and subtraction of the scattering from the empty cell were made. No correction for multiple scattering was made because we estimated the multiple scattering to be not large due to the thickness of sample. The dynamic structure factor  $S(Q, E)$  was derived from the time of flight spectra. Because the incoherent neutron scattering length of H is much larger than that of D, C, and O, the obtained spectra are mainly attributable to incoherent scattering from H atoms. In this study the contribution of the hydrogen atoms in hydroxyl group of alcohol can be ignored because the fraction of hydrogen atoms in hydroxyl group of alcohol molecules to all hydrogen atoms in a sample is small for the dilute solutions studied here, that is, the fraction is ranged from 0.01 to 0.05 for the solution of  $x_p = 0.02$ –0.10. Hence, the self-diffusion property of water molecules can be found out from the  $S(Q, E)$ .

### III. ANALYTICAL METHOD

In order to analyze the dynamics of water molecules in the alcohol-water mixtures, the dynamical structure factor

$S(Q, E)$  was fitted with functions of two models, i.e., jump diffusion and relaxing cage models. We assumed a decoupling of vibrational, translational, and rotational motions of the molecules for analytical model.

The intermediate scattering function  $F(Q, t)$ , which is the Fourier transform of the dynamic structure factor  $S(Q, E)$ , for jump diffusion model<sup>16</sup> is written as

$$F(Q, t) = \exp\left(-\frac{\langle u^2 \rangle Q^2}{3}\right) \exp\left[-\frac{D_T Q^2}{1 + D_T Q^2 \tau_0} t\right] \times \left\{ j_0^2(Qd) + \sum_{l=1} (2l+1) \times j_l^2(Qd) \exp\left[\frac{-l(l+1)}{2} \frac{t}{\tau_1}\right] \right\}. \quad (1)$$

The  $F(Q, t)$  consists of three factors. The first one, which represents the vibrational relaxation, has the form of Debye–Waller factor and contains the root mean square of the vibrational amplitude  $\langle u^2 \rangle^{1/2}$  of water molecules. The second factor corresponds to the translational relaxation, which is the exponential form. The coefficient of  $t$ , which corresponds to the peak width of  $S(Q, E)$ , contains parameters of a diffusion coefficient  $D_T$  and a residence time  $\tau_0$ . The last factor represents the rotational relaxation. The  $j_l(Qd)$  is the  $l$ th order spherical Bessel function and  $d$  is the O–H distance, 0.98 Å is used as  $d$  in this study. This factor is hardly effective in low  $Q$  region.

For the relaxing cage model<sup>16,17</sup> the mode coupling effect is considered so the translational and rotational motions are described by a stretched exponential characterized by the relaxation time  $\tau$  and the stretched exponent  $\beta$ . As a consequence, the intermediate scattering function is written as

$$F(Q, t) = \exp\left(-\frac{\langle u^2 \rangle Q^2}{3}\right) \exp\left[-\left(\frac{t}{\tau_T(Q)}\right)^{\beta_T(Q)}\right] \times \left\{ j_0^2(Qd) + \sum_{l=1} (2l+1) \times j_l^2(Qd) \exp\left[\frac{-l(l+1)}{2} \left(\frac{t}{\tau_R(Q)}\right)^{\beta_R(Q)}\right] \right\}. \quad (2)$$

The translational average relaxation time  $\tau_{av}(Q)$  can be derived using the values of  $\tau_T(Q)$  and  $\beta_T(Q)$  as

$$\tau_{av}(Q) = \int_0^\infty dt \exp\left[-\left(\frac{t}{\tau_T(Q)}\right)^{\beta_T(Q)}\right] = \frac{\tau_T(Q)}{\beta_T(Q)} \Gamma\left[\frac{1}{\beta_T(Q)}\right]. \quad (3)$$

where  $\Gamma(x)$  is the gamma function. The parameter  $\tau_{av}(Q)$  can be used to estimate a diffusion coefficient  $D$ . The following empirical relationship between  $1/\tau_{av}(Q)$  and  $D$  also hold validity for the cage model,

$$\frac{1}{\tau_{av}(Q)} = DQ^2. \quad (4)$$

Here, the diffusion coefficient  $D$  can be derived from a slope of the plot of  $1/\tau_{av}(Q)$  versus  $Q^2$ .

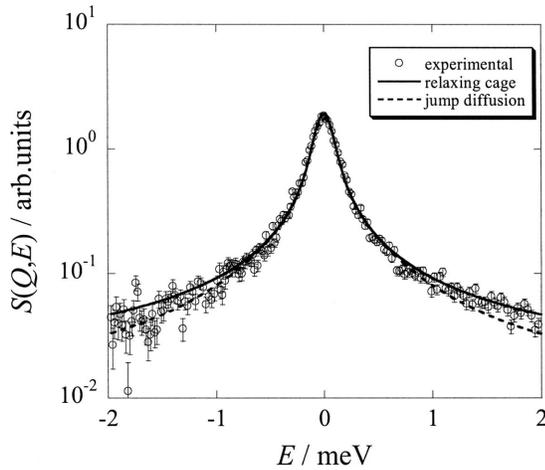


FIG. 1. The dynamic structure factor  $S(Q, E)$  for the solution of  $x_p=0.167$  at  $25^\circ\text{C}$  and  $Q=1.363\text{ \AA}^{-1}$ . Experimental data: open circles. Relaxing cage model fit curve: solid line, jump diffusion model fitting curve: dashed line.

The fitting of the experimental  $S(Q, E)$  was carried out by varying the parameters  $\tau_T(Q)$  and  $\beta_T(Q)$  in the translational relaxation part of Eq. (2). On the other hand, the parameters in the rotational relaxation part of Eq. (2) were fixed as  $\tau_R(Q)=45\text{ ps}$  and  $\beta_R(Q)=0.6$ , which correspond with the values by A. Yoshida *et al.*<sup>7</sup> and those of our preliminary fitting  $\tau_R(Q)=45\pm 1\text{ ps}$  and  $\beta_R(Q)=0.6\pm 0.1$ . The energy range of fitting was  $-2\text{ meV}\leq E\leq 2\text{ meV}$  and the  $Q$  range was  $0.376\text{--}2.504\text{ \AA}^{-1}$ .

#### IV. RESULTS

The experimental dynamic structure factor  $S(Q, E)$  for the solution of  $x_p=0.167$  at  $25^\circ\text{C}$  and  $Q=1.363\text{ \AA}^{-1}$  is shown by open circles in Fig. 1, in which error bars show the statistical error, the fitting curves of the relaxing cage and the jump diffusion models are also shown by solid and dashed lines, respectively. The logarithmic scale is used for vertical axis to emphasize the difference between the two fitting models in the large energy transfer region. The correspondences between the experimental data and the calculated curves are good for both models. However the correspondence in high energy transfer region (tail parts) seems to be better for the cage relaxation model than that for the jump diffusion model. The weighted sum of squared residual error  $R$  for jump diffusion model is about two times larger than that of relaxing cage models for each composition. The fitting with relaxing cage model is slightly good and hereafter the results with the relaxing cage model is mainly described. The plots of parameters  $\tau_T(Q)$  and  $\beta_T(Q)$  as a function of  $Q$  are shown in Figs. 2(a) and 2(b). The parameters  $\tau_T(Q)$  and  $\beta_T(Q)$  show obvious dependence both on  $Q$  and  $x_p$ . The values of  $\tau_T(Q)$  increase with increasing alcohol concentration, while the values of  $\beta_T(Q)$  decrease at the same time. Both  $\beta_T(Q)$ 's for pure water and the solution of  $x_p=0.167$  show the similar trends. It is noticeable that the  $\beta_T(Q)$  shows anomalous behavior at  $Q\sim 1.5\text{ \AA}^{-1}$ . This may indicate that there is an interesting dynamic structural property at a characteristic  $Q=1.363\text{ \AA}^{-1}$ .

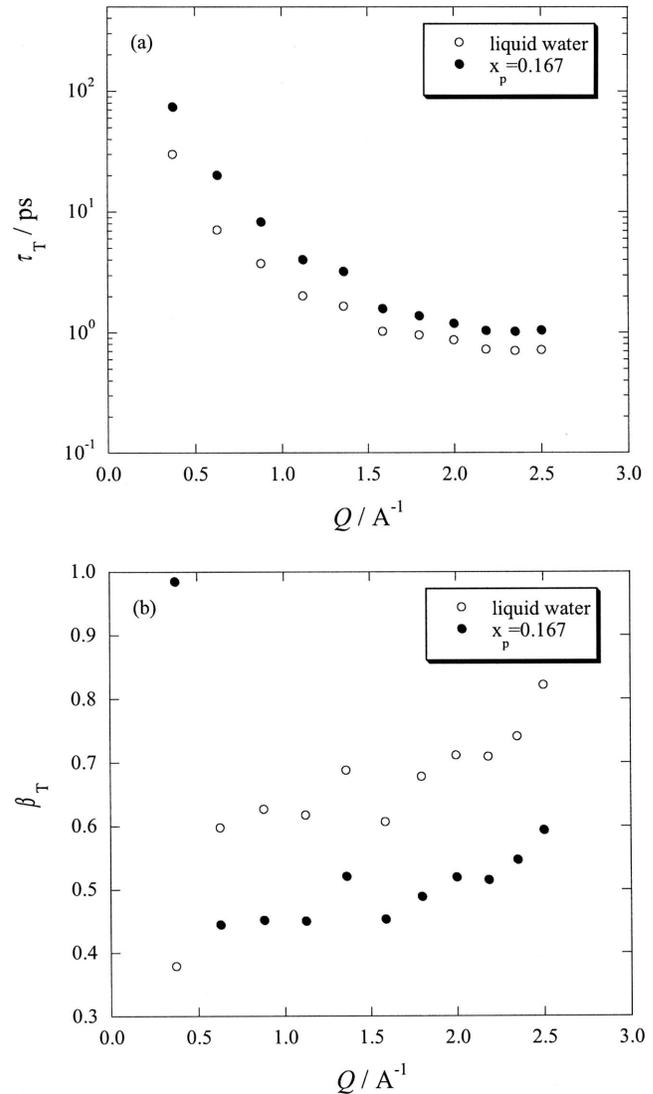


FIG. 2. Plots of the translational relaxation time  $\tau_T(Q)$  and the translational stretched exponent  $\beta_T(Q)$  for the relaxing cage model as a function of  $Q$  for pure water (open circles) and the solution of  $x_p=0.167$  (closed circles) at  $25^\circ\text{C}$ .

Figure 3 shows the plots of  $1/\tau_{av}(Q)$  as a function of  $Q^2$  for the water (open circles) and for the mixture of  $x_p=0.167$  (closed circles), which shows the linear correlation at low  $Q$  region. The diffusion coefficient  $D$  can be derived from the slope of the plot of Fig. 3 in low  $Q$  region by using Eq. (4). Figure 4 shows the plot of the diffusion coefficient  $D$  as a function of  $x_p$  derived from the relaxing cage model (open circles) and jump diffusion model (closed circles). The  $D$  from both two models decreases with increasing the alcohol concentration  $x_p$ . The values for jump diffusion model are systematically larger than those for the relaxing cage model, as seen in Fig. 4. To examine the validity of the analyses by two models, we compare the values of  $D$  for pure water with those reported by other researchers<sup>19–23</sup> in Table II. The value derived from the relaxing cage model corresponds with the reported values, while that derived from the jump diffusion model quantitatively deviates from other data. The diffusion coefficients of water molecules in *n*-propyl alcohol-water mixture reported by Hawlicka and

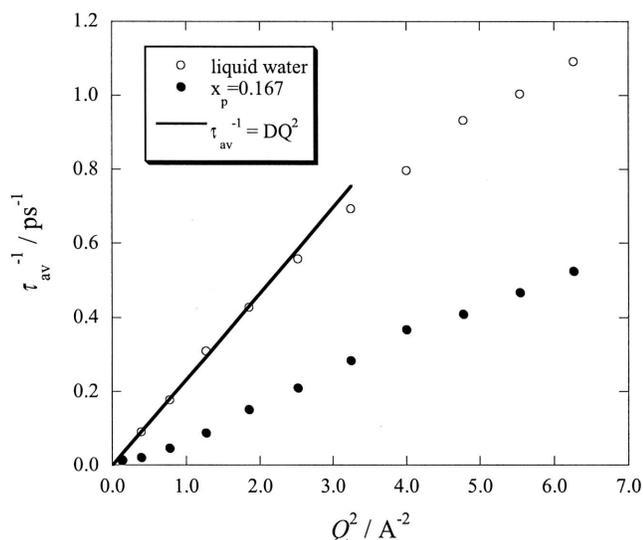


FIG. 3. The  $Q^2$  dependence of the inverse of the averaged translational relaxation time  $1/\tau_{av}(Q)$  for the relaxing cage model for pure water (open circles) and the solution of  $x_p=0.167$  (closed circles) at 25 °C. Solid line shows the relation of  $1/\tau_{av}(Q)=DQ^2$ , where  $D=0.232 \text{ \AA}^2 \text{ ps}^{-1}$  for pure water.

Grabowski<sup>24</sup> are shown in Fig. 4 by triangles. The composition dependence of the diffusion coefficient derived by the relaxing cage model correspond well with these experimental data, as shown in Fig. 4. The preliminary data of the spectrum obtained by high-resolution mode AGNES show better corresponding in the value of  $D$  derived by the relaxing cage model, we conclude that the relaxing cage model presents more reasonable dynamical properties of water molecules in water-alcohol mixtures.

## V. DISCUSSION

In the previous paper<sup>3</sup> we have suggested that there are only two states of water molecules, i.e., bulk state and hy-

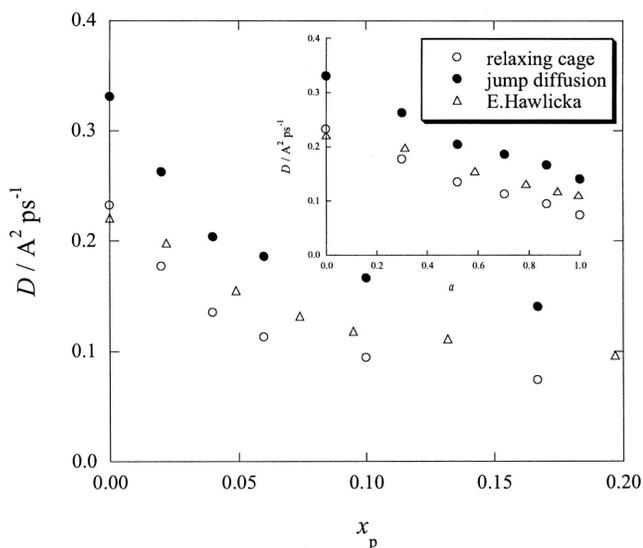


FIG. 4. The plot of diffusion coefficient  $D$  as a function of  $x_p$  derived by the relaxing cage model (open circles) and the jump diffusion model (closed circles) and that reported by Hawlicka and Grabowski (Ref. 24) (open triangles). The plot of  $D$  as a function of  $\alpha$  is also drawn (inset).

drophobic hydrating state, in  $n$ -propyl alcohol-water mixture below  $x_p=0.167$ . In the solution of  $x_p=0.167$ , most water molecules are hydrophobic hydrated to  $n$ -propyl alcohol clusters. Thus, we regard the values of diffusion coefficients  $D$  of liquid water  $x_p=0.0$  and the solution of  $x_p=0.167$  as those for water molecules in bulk state and hydrophobic hydration state, respectively. It is notable that the value of  $D$  for  $x_p=0.167$  is smaller than that for liquid water, which suggests that the diffusion motion of hydrophobic hydrating water molecules is slower than that of bulk water molecules.

The behavior of  $\langle u^2 \rangle^{1/2}$  is shown in Fig. 5 as a function of the fraction of hydrophobic hydrating water molecules  $\alpha$ . The  $\langle u^2 \rangle^{1/2}$  linearly increases with  $\alpha$ . The plot of  $D$  as a function of fraction of the hydrophobic hydrating water molecules  $\alpha$  is also drawn in an inset frame. Diffusion coefficient  $D$  also shows linear relation to  $\alpha$ , as shown in an inset of Fig. 4. Consequently the following results is indicated: in the solution of  $x_p=0.0-0.167$ , where  $\alpha$  changes from 0.0 to 1.0,  $D$ , and  $\langle u^2 \rangle^{1/2}$ , or other diffusion properties, can be estimated from the interpolation between the bulk and hydrophobic hydrating states. That is, when we consider the diffusional properties of  $n$ -propyl alcohol-water mixture, we have to only obtain the diffusional parameters for pure water and the solution of  $x_p=0.167$  then the corresponding parameters for intermediate concentration,  $0.0 < x_p < 0.167$ , can be estimated by a linear combination of the values for two states. This result strongly supports the validity of the two state approximation for water molecules.

The parameter  $\tau_T(Q)$  expresses relaxation of each water molecules. Figure 6(a) shows the  $\alpha$  dependence of  $\tau_T(Q)$  averaged over  $Q=0.632-2.504 \text{ \AA}^{-1}$ . The  $\tau_T(Q)$  increases linearly with increasing  $\alpha$ . This result is reasonable as previous discussion. For further analysis, the physical meaning of the parameter  $\beta_T(Q)$ , which is characteristic parameter of the relaxing cage model, was considered. The  $\beta$  dependence of the stretched exponential function,  $G(t)=\exp\{-(t/\tau)^\beta\}$ , was examined. For smaller  $\beta$ ,  $G(t)$  has longer tail in a large  $t$  region. When the value of  $\beta_T(Q)$  decreases in Eq. (2), the tail of  $F(Q,t)$  is extended, which means that some part of the water molecules surrounding the alcohol come to be staying longer time. Thus, comparison between the  $D$  for pure water and the solution of  $x_p=0.167$  shown in Fig. 4 shows that relaxation for hydrophobic hydrating water molecules is slower than that for bulk water molecules, which is one of the origin of smaller  $\beta_T(Q)$  for the solution of higher  $x_p$ . The parameters  $\beta_T(Q)$  averaged from  $Q=0.632$  to  $2.504 \text{ \AA}^{-1}$  are plotted against  $\alpha$  in Fig. 6(b). The behavior of averaged  $\beta_T(Q)$  also shows linear correlation with  $\alpha$  as the  $D$ ,  $\langle u^2 \rangle^{1/2}$ , and  $\tau_T(Q)$ , so the two state approximation for water molecules is once again certified. As a conclusion, the parameter  $\beta_T(Q)$  adequately expresses the effect of hydrophobic hydration of the cage relaxation, and the averaged values of  $\beta_T(Q)$  for bulk and hydrophobic hydrating water molecule are estimated to be 0.7 and 0.5, respectively.

In our previous paper<sup>25</sup> we have also succeeded in reproducing the excess molar volume of  $t$ -butyl alcohol-water mixture by using the same volume contraction/expansion parameters of mixing as those for  $n$ -propyl alcohol-water mixture. This may indicate that the states of water molecules that

TABLE II. Comparison of the values of diffusion coefficients  $D$  for pure water at 25 °C derived from two models of present study with those reported by other investigators (Refs. 19–23).

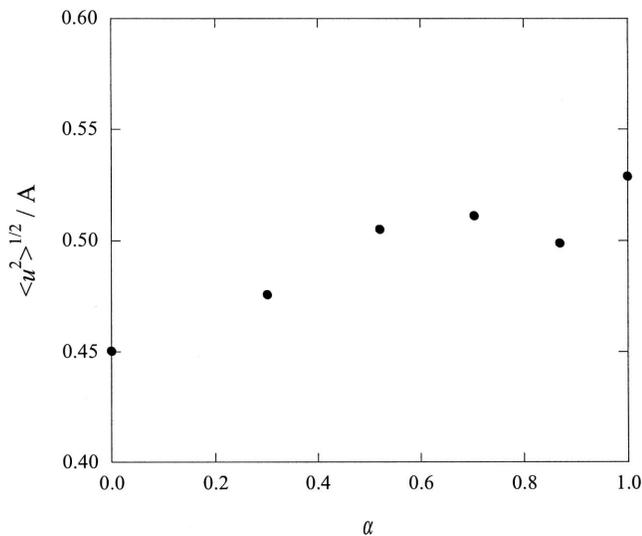
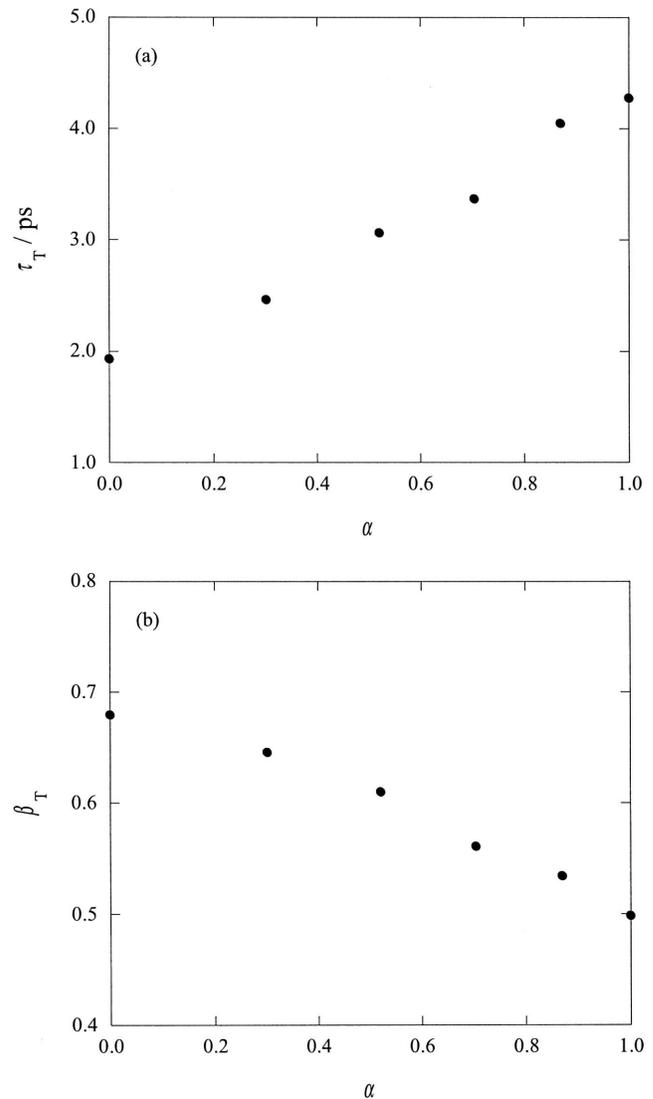
References	Experimental technique	Diffusion coefficient $D$ ( $\text{\AA}^2 \text{ps}^{-1}$ )
Relaxing cage model	QENS	0.232
Jump diffusion model	QENS	0.331
Wang <i>et al.</i> <sup>a</sup> (1952)	HDO tracer in capillary tube	0.234
	HTO tracer in capillary tube	0.244
	H <sub>2</sub> O <sup>18</sup> tracer in capillary tube	0.266
Wang <i>et al.</i> <sup>b</sup> (1965)	H <sub>2</sub> O <sup>18</sup> tracer in capillary tube	0.257
Gillen <i>et al.</i> <sup>c</sup> (1972)	NMR spin echo measurement	0.223
Tanaka <sup>d</sup> (1978)	D <sub>2</sub> O tracer in sintered glass diaphragm cell	0.227
	H <sub>2</sub> O <sup>18</sup> tracer in sintered glass diaphragm cell	0.227
Harris and Woolf <sup>e</sup> (1979)	NMR spin echo measurement	0.219

<sup>a</sup>Reference 19.<sup>b</sup>Reference 20.<sup>c</sup>Reference 21.<sup>d</sup>Reference 22.<sup>e</sup>Reference 23.

are hydrophobically hydrating to various alcohol clusters are the same and independent of the alcohol species. If this prediction is right, the diffusional properties of one water molecule, such as diffusion coefficient, and the parameters  $\tau_T(Q)$  and  $\beta_T(Q)$ , should be the similar functions for the aqueous solutions of various alcohols such as ethyl alcohol, *n*-propyl alcohol, and *t*-butyl alcohol.

## VI. CONCLUSION

The best fitting of the QENS spectra of *n*-propyl alcohol-water mixtures is obtained by using the relaxing cage model. For the relaxing cage model, translational relaxation time  $\tau_T(Q)$  and stretched exponent  $\beta_T(Q)$  show the obvious dependence both on  $Q$  and alcohol concentration  $x_p$ . The values of  $\tau_T(Q)$  increase with increasing  $x_p$ , while the values of  $\beta_T(Q)$  decrease at the same time. The  $Q$  dependence of  $\beta_T(Q)$  changes around  $Q \sim 1.5 \text{ \AA}^{-1}$ . The averaged relaxation time  $\tau_{av}^{-1}(Q)$  derived from parameters  $\tau_T(Q)$  and  $\beta_T(Q)$

FIG. 5. The root-mean-square displacement  $\langle u^2 \rangle^{1/2}$  as a function of  $\alpha$ .FIG. 6. Averaged translational relaxation time  $\tau_T(Q)$  and stretched exponent  $\beta_T(Q)$  as a function of  $\alpha$ .

shows linear correlation against  $Q^2$ . Consequently, the diffusion coefficients  $D$  could be derived from the slope at low  $Q$  region. The  $D$  derived from both the relaxing cage model and the jump diffusion model decreases with increasing alcohol concentration  $x_p$ . The values of the relaxing cage model are in better agreement with experimental data than that of jump diffusion model. Therefore, we decided that the relaxing cage model is more reasonable physical model for the motion of water molecules in water-alcohol mixture.

The water molecules can be divided roughly into two states in water-rich region; water molecules in bulk state and in hydrophobic hydration state. The  $D$  depends linearly on  $\alpha$ . Furthermore, other parameters such as  $\tau_T$ ,  $\beta_T$ , and  $\langle u^2 \rangle^{1/2}$  also show linear correlation against  $\alpha$ . These facts indicate that the two state approximation is satisfied in water-rich concentration region.

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