The Journal of Physical Chemistry A

VOLUME 103, NUMBER 34, AUGUST 26, 1999

ARTICLES

Pressure Effect on Hydrophobic Hydration: Rotational Dynamics of Benzene

Chihiro Wakai, Nobuyuki Matubayasi, and Masaru Nakahara*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received: January 5, 1999; In Final Form: June 10, 1999

Deuteron nuclear magnetic resonance spin−lattice relaxation times T_1 have been measured for deuterated benzene molecules (C_6D_6) in dilute solutions of water (H_2O) and methanol at temperatures of 1, 2, 5, 15, and 30 °C and pressures up to 300 MPa. At the higher temperatures of 15 and 30 °C, the rotational correlation time τ_{2R} of C_6D_6 in the aqueous solution (H_2O) increases with pressure, whereas the τ_{2R} of D_2O decreases. This difference is interpreted in terms of the compression mechanism involving the packing effect and the orientational dependence of intermolecular interactions. At lower temperatures, the pressure dependence of the τ_{2R} of C_6D_6 at initial compression is smaller. Especially, at the lowest temperature of 1 °C, the τ_{2R} of C_6D_6 in the aqueous solution is very weakly dependent on the pressure up to 100 MPa. This implies that a strong hydration shell due to the hydrophobic effect resists compression up to 100 MPa and that the rotational mobility of C_6D_6 is not affected by the pressure. When the pressure is raised beyond 100 MPa, the pressure dependence of the τ_{2R} at 1 °C is similar to those at the higher temperatures of 15 and 30 °C and the hydration shell is relatively weak. For the methanol solution, in contrast, the τ_{2R} of C_6D_6 increases monotonically with pressure both at 1 and 30 °C. The activation energies of the τ_{2R} of C_6D_6 in the aqueous solution and D_2O in pure liquid exhibit anomalous reductions as functions of the pressure. The reduction of the activation energy is accounted for by the pressure-induced weakening of hydrogen bonds between water molecules around the solute benzene.

1. Introduction

Hydrophobic hydration plays a key role in understanding biologically important chemical processes in aqueous solution.[1] Recently, its dynamic properties, especially rotational dynamics of a hydrophobic solute and hydrating water molecules, have been studied over a wide temperature range.[2−9] It has been reported that, at lower temperatures, the rotational motion of a hydration shell water is hindered because of the increase of the hydrogen bonds and that in the clathrate-like hydration shell, solute molecules can reorient with rather weak frictions.[2,3]

In addition to temperature, pressure is a variable to control the nature of solutions. The study of pressure effects reveals the intermolecular interaction effect on the hydrophobic hydration at a constant kinetic energy (temperature). For the pure solvent, it is well-known that the hydrogen bonds in water are disrupted and distorted by pressure.[10] For the solution, on the other hand, it is still to be investigated how the hydration shell responds to pressure variation. In this paper, we will elucidate the strength of the hydration shell by focusing on the pressure effect on the rotational mobilities of both the hydrophobic solute benzene and the solvent water.

NMR studies on the pressure effect of the hydrophobic hydration have traditionally been restricted to freely soluble polar molecules such as alcohols[11,12] and tetraalkylammonium salts,[13,14] for which an apolar and hydrophobic moiety is

---

* To whom correspondence should be addressed. Fax: +81-774-38-3070. E-mail: nakahara@scl.kyoto-u.ac.jp.

10.1021/jp990044y CCC: $18.00

TABLE 1: Rotational Correlation Time (τ_{2R}) of C_6D_6 in the Aqueous Solution at 1, 2, 5, 15, and 30 °C as a Function of Pressure

	τ_{2R} (ps)				
p (MPa)	1 °C	2 °C	5 °C	15 °C	30 °C
0.1	3.58 ± 0.04	3.44 ± 0.01	3.21 ± 0.04	2.57 ± 0.03	1.90 ± 0.01
50	3.62 ± 0.16	3.50 ± 0.04	3.34 ± 0.10	2.69 ± 0.13	2.04 ± 0.01
100	3.58 ± 0.10	3.64 ± 0.04	3.45 ± 0.10	2.86 ± 0.05	2.11 ± 0.02
150	3.82 ± 0.04	3.78 ± 0.02	3.69 ± 0.11	3.08 ± 0.05	2.24 ± 0.01
200	4.04 ± 0.12	3.96 ± 0.03		3.08 ± 0.16	2.37 ± 0.02
250	4.21 ± 0.05			3.30 ± 0.09	2.45 ± 0.02
300	4.54 ± 0.18			3.47 ± 0.08	2.61 ± 0.02

combined with a polar or ionic one as a solubility anchor. In this case, hydrophobic effects may be mixed together with hydrophilic ones and it is not straightforward to separate pure hydrophobic effects. To avoid this type of difficulty, benzene is used as a pure hydrophobic solute in the present work.

Rotational mobility is much more sensitive to the microscopic environment around solute molecules than the translational one[2,3,15−19] and is a good probe to the hydrophobic hydration.[2,3,5] We have studied the rotational dynamics of a solitary water molecule (D_2O) as a polar solute in polar and apolar solvents and showed that the rotational mobility is controlled by the attractive interaction between the solute and the solvent.[15] Also, for a benzene molecule as an apolar solute in organic solvents, we have found a positive correlation between the dissolution enthalpy, a measure of the strength of the solute−solvent interaction, and the slope of the plots of the rotational correlation time against the solvent viscosity divided by temperature.[16,17] Thus, it is insightful to study rotational dynamics of hydrophobic hydration by NMR. For benzene in aqueous solution, we have shown that at low temperatures including supercooled regions, the rotational motion of the solute benzene is rather accelerated in a clathrate-like hydration shell.[2,5] In this work, from the pressure dependence of the rotational mobility of benzene in normal liquid conditions, we will show that at higher temperatures a hydration shell is vulnerable to pressure and that at lower temperatures a strong hydration shell exists, in which a benzene molecule can reorient with scarcely feeling the pressure effect.

In the following section, we show the experimental procedure. In section 3, we analyze the pressure dependences of the rotational correlation times τ_{2R} of benzene and heavy water (D_2O) and discuss the compression effects on the rotational mobility of benzene and heavy water molecules. To clarify the anomalous pressure dependence of the τ_{2R} of benzene in aqueous solution, the pressure dependence of the τ_{2R} of benzene in methanol is also shown. In section 4, we discuss the temperature dependence of the pressure effect on the τ_{2R} of benzene and show the existence of a strong hydration shell which resists the compression. In section 5, we compare the activation volumes and the activation energies of the rotational motion of benzene molecules in aqueous solution, methanol solution, and neat benzene. The partial molar compressibility is also discussed. The paper is concluded in section 6.

2. Experimental Section

Benzene-d_6 was obtained from CEA (Commissariat a L'Energie Atomique). Water was purified to a specific conductance of 5.6 × 10^{-6} S m^{-1} by using the Milli-Q Labo. filter system (Milli-Q Pore). Methanol was obtained from Nacalai and used after dried by molecular sieves 3A. Water and benzene-d_6 were mixed by a magnetic stirrer for several days at 22 °C. The concentration of the solution saturated under ambient condition was 23 mM (M = mol dm^{-3}).[20] The solution of benzene-d_6 in methanol was prepared by weight, and the concentration was 100 mM.

We used an NMR spectrometer (JNM-EX270; JEOL) equipped with an Oxford superconductor magnet (6.35 T). The magnet has a wide bore so as to accommodate the specially designed high-pressure probe.[18,21] The resonance frequency for deuteron is 41 MHz. The temperature was controlled to 0.1 °C. The pressure was generated by a hand pump, monitored by a Bourdon gauge, and transferred to the NMR probe by stainless tubes. The uncertainty of pressure was within ±0.5 MPa.

We measured the deuteron spin−lattice relaxation times T_1 for C_6D_6 in H_2O and CH_3OH. The T_1 measurement was started more than 30 min after the pressure variation with an interval of 50 MPa so that the evolved heat was ensured to dissipate completely. The T_1 values were determined by the inversion−recovery method with the $\pi-t-\pi/2$ pulse sequence. The number of delay times t was 20. The longest delay time exceeded $7T_1$. We accumulated the free induction decays 20 times. The resulting S/N ratios in the recovered spectra were 50. The number of sampling points was 8192, and the observed frequency range was 500 Hz so that the digital resolution was 0.122 Hz. The $\pi/2$ pulse width was 29.5 μs.

The rotational correlation time τ_{2R} was calculated as follows. The deuteron has the nuclear spin quantum number $I = 1$, and the spin−lattice relaxation is governed by the quadrupole mechanism. At the extremely narrowing condition ($\tau_{2R}\omega \ll 1$; ω is the resonance frequency), the relaxation rate $1/T_1$ is related to the τ_{2R} as

$$\frac{1}{T_1} = \frac{3\pi^2}{2}\left(\frac{e^2Qq}{h}\right)^2 \tau_{2R} \qquad (1)$$

where e^2Qq/h is the quadrupole coupling constant (QCC), which is a measure of the strength of the interaction between the quadrupole moment of a nucleus (eQ) and the electric field gradient at the nucleus (eq). The correlation time τ_{2R} is the time integral of the time correlation function of the second-order orientation of the C−D axis. The QCC value we used is 193 kHz.[16] Here, we neglect the anisotropy of the electric field gradient because the QCC value for the D nucleus in C_6D_6 is determined almost entirely by the covalent σ electrons and the distribution of the σ electrons is almost cylindrical on the C−D axis. In addition, due to the σ nature of the electrons determining the QCC, the QCC value is assumed to be independent of the temperature and the pressure.

In Table 1, the τ_{2R} values of benzene in the aqueous solution at 1, 2, 5, 15, and 30 °C are listed. In addition, those in the methanol solution at 1 and 30 °C are listed in Table 2.

3. Comparison of Rotational Mobility of Benzene in Benzene, Water, and Methanol

Our focus is on the pressure dependence of the rotational mobility of benzene in the aqueous solution. In Figure 1, the

TABLE 2: Rotational Correlation Time (τ_{2R}) of C_6D_6 in the Methanol Solution at 1 and 30 °C as a Function of Pressure

	τ_{2R} (ps)	
p (MPa)	1 °C	30 °C
0.1	1.27 ± 0.01	0.980 ± 0.005
50	1.50 ± 0.01	1.15 ± 0.01
100	1.73 ± 0.01	1.29 ± 0.01
150	1.96 ± 0.01	1.45 ± 0.01
200	2.18 ± 0.01	1.60 ± 0.01
250		1.76 ± 0.01
300		1.93 ± 0.01

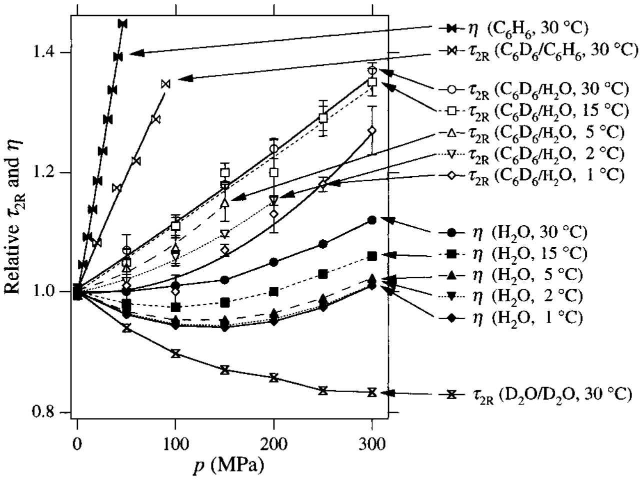

Figure 1. Pressure dependences of the rotational correlation times (τ_{2R}) of benzene in pure liquid, benzene in the aqueous solution (H_2O), and heavy water (D_2O) in pure liquid, and the solvent viscosity (η) at 1, 2, 5, 15, and 30 °C. Viscosity data of water and benzene are from refs 22 and 25, respectively. In the symbol X/Y, X and Y denote the solute and the solvent, respectively.

τ_{2R} values normalized relative to the atmospheric ones of the solute benzene (C_6D_6) and the solvent water (D_2O) molecules are plotted against pressure at 1, 2, 5, 15, and 30 °C, together with the normalized viscosity η of water (H_2O).[22]

First we will discuss the pressure dependences of the τ_{2R} of benzene at the higher temperatures of 15 and 30 °C. The τ_{2R} of benzene in the aqueous solution increases steadily with pressure at 15 and 30 °C. In other words, benzene molecules in the aqueous solution *reorient slower* with pressure. This pressure dependence is remarkably different from that of water molecules (D_2O). The τ_{2R} of D_2O decreases and water molecules *reorient faster* with pressure, in agreement with Jonas et al.[10] In other words, the solute benzene and the solvent water molecules involve opposite pressure dependences in terms of the rotational mobility. This discrepancy is a manifestation of the unique liquid structure of water. The pressure increases the coordination number of a water molecule with making the local environment less tetrahedral, while the oxygen−oxygen distance of a hydrogen bonding pair of water molecules does not change.[23,24] Thus, compression induces a decrease in the angular order of the local environment of water. Figure 1 suggests that this angular compression acts as the factor to control the pressure dependence of the rotational mobility of water. For the hydrophobic solute benzene, on the other hand, Figure 1 suggests that the packing effect is the key factor to determine the pressure dependence of the rotational mobility. With regard to the packing effect, it is of interest to note the pressure dependence of the τ_{2R} of benzene in its pure liquid. In a previous paper,[18] we have studied the pressure dependences of the τ_{2R} of benzene in its pure liquid. As shown in Figure 1, the pressure dependence of the τ_{2R} of benzene is stronger in the pure liquid than in the aqueous solution. This implies that the packing effect in pure benzene is stronger than that in the aqueous solution because the pressure dependence of the number density of benzene is much larger than that of water. In both solvents, the packing effect is a main factor in controlling the rotational dynamics of the solute benzene.

We will compare the pressure dependence of the τ_{2R} of benzene in the aqueous solution with that of the solvent viscosity. According to the Stokes−Einstein−Debye (SED) theory based on the hydrodynamic continuum model, the τ_{2R} is proportional to the solvent viscosity divided by temperature,

$$\tau_{2R} = \frac{4\pi R^3}{3k_B}\frac{\eta}{T} \tag{2}$$

where R is the radius of the solute, k_B is the Boltzmann constant, η is the solvent viscosity, and T is the temperature. According to this model, when the viscosity is varied by pressure at constant temperature, the τ_{2R} is proportional to the viscosity:

$$\frac{\tau_{2R}(p)}{\tau_{2R}(0.1)} = \frac{\eta(p)}{\eta(0.1)} \tag{3}$$

where p and 0.1 are the pressures in MPa. As seen in Figure 1, the τ_{2R} *increases* with pressure. With the elevation of pressure, however, the solvent viscosity decreases and has a minimum at 100 MPa and increases with pressure at pressures higher than 100 MPa. Therefore, at initial compression, the hydrodynamic model is broken not only quantitatively but also qualitatively even for the solute benzene, which has no such strong solute−solvent interaction as hydrogen bonds.

For pure liquid benzene, on the other hand, both the normalized τ_{2R} value[18] of benzene and the normalized viscosity[25] increase monotonically with pressure as shown in Figure 1. The hydrodynamic model is thus valid qualitatively for such a rather simple liquid as benzene. The pressure dependence of the τ_{2R} is a little smaller than that of the solvent viscosity. This has been explained by the difference in the length scales of the viscosity and the rotational motion; the length scale is longer for the viscosity than for the rotational correlation time.[18] The pressure affects the viscosity more strongly.

To further clarify the anomalous response of the solvent water to compression, methanol was used as a reference solvent. Methanol does not make a clathrate-like solvation shell around benzene despite its hydrogen-bonding nature. In Figure 2, the pressure dependences of the normalized τ_{2R} of benzene in the methanol solution and the normalized viscosity of methanol[26] are shown at 1 and 30 °C. The τ_{2R} of benzene in the methanol solution increases with pressure at 1 and 30 °C, in agreement with benzene in the aqueous solution at 15 and 30 °C. This indicates that the tighter packing of the solvation shell slows down the rotational motion of a solute benzene. The viscosity of methanol also increases with pressure, unlike that of water. For the solvent methanol, the hydrodynamic model is valid qualitatively and the pressure dependence of the τ_{2R} is a little smaller than that of the viscosity, in agreement with pure liquid of benzene. Therefore, the difference in the pressure dependence between the τ_{2R} of benzene in aqueous solution and organic solvents is due not to the hydrogen bonding but to the hydration structure.

4. Anomalous Pressure Dependence at Low Temperature

As seen in the preceding section, at the higher temperatures of 15 and 30 °C, a benzene molecule reorients slower at a higher

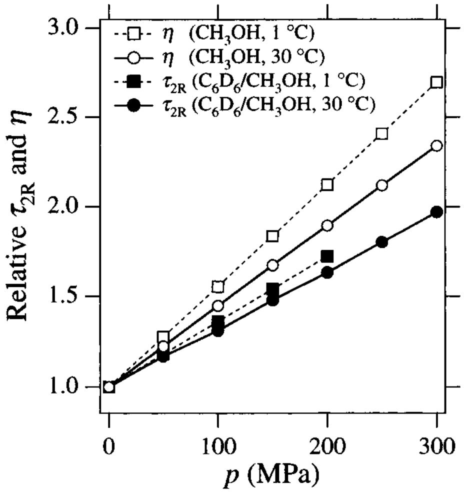

Figure 2. Pressure dependences of the rotational correlation times (τ_{2R}) of benzene in the methanol solution and the solvent viscosity (η) at 1 and 30 °C. Viscosity data are from ref 26. In the symbol X/Y, X and Y denote the solute and the solvent, respectively.

pressure due to the packing effect. At temperatures lower than 15 °C, on the other hand, anomalous pressure dependences are observed for the rotational mobility of the solute benzene in the hydration shell. In Figure 1, the τ_{2R} values for benzene in the aqueous solution (H_2O) normalized to those at 0.1 MPa are plotted against pressure at the lower temperatures of 1, 2, and 5 °C together with the normalized viscosity of water (H_2O).[22] At a lower temperature, the pressure dependence at initial compression is smaller. Especially, at 1 °C the τ_{2R} for benzene in the aqueous solution is very weakly dependent on the pressure up to ~100 MPa. This anomalous pressure dependence is not explained, even qualitatively, by the hydrodynamic model. At any temperature, the viscosity decreases with pressure at initial compression while the τ_{2R} increases at 2 and 5 °C. The temperature dependence of the pressure effect on the τ_{2R} at initial compression is much larger than that of the viscosity.

Concerning the temperature effect at the atmospheric pressure, we have shown that the rotational mobility of water molecules in the hydration shell is strongly hindered at lower temperature.[2,4] For example, at a temperature of 0 °C, the τ_{2R} for the shell water is 3 times larger than that for the bulk water, whereas at 30 °C, the τ_{2R} for the shell water is larger than that for the bulk water by only 50%. This shows that the strength of the hydration shell is sensitive to the temperature. When the pressure dependence of τ_{2R} is concerned in Figure 1, its interpretation is also possible by employing the concept of the hydrophobic hydration shell around the solute benzene. The pressure dependence of the τ_{2R} of benzene at the higher temperature of 30 °C indicates that the hydrogen bonding among water molecules in the hydrophobic hydration shell is weak and that the hydration shell is vulnerable to the pressure. At the higher temperatures of 15 and 30 °C, the rotational dynamics of the solute benzene is controlled mainly by the packing effect. At the lowest temperature of 1 °C, on the other hand, the initial invariance of the τ_{2R} indicates that a strong hydration shell around benzene resists the compression up to ~100 MPa and that the solute benzene can reorient without the effect of tighter packing in the strong hydration shell.

This anomalous pressure dependence is consistent with the temperature-variable measurements of the τ_{2R} for the solute benzene.[2] It has been reported[2] that at a lower temperature than 12 °C, the τ_{2R} of a benzene molecule in the aqueous solution is *smaller* than that of water (a benzene molecule can reorient *faster* than a water molecule), although the benzene molecule is *larger* in size than the water molecule. At a higher temperature than 12 °C, the τ_{2R} of a benzene molecule in the aqueous solution is larger than that of water, in accordance with the size. This anomaly reported in ref 2 is caused by the superiority of the hydrogen bonding effect to the excluded volume effect on the rotational mobility. As a result of the hydrogen bonding among water molecules in the hydrophobic hydration shell, the rotational mobility of the solute benzene is rather accelerated. In addition, when the clathrate hydrate, which is the hydrophobic hydration shell itself, is formed in supercooled regions, the rotational motion of benzene in the clathrate hydrate cage gets 3 times faster than that in the aqueous solution.[3,5] Therefore, the anomalous pressure dependence of the τ_{2R} at 1 °C and the temperature dependence of the τ_{2R} at the atmospheric pressure for the solute benzene are both considered to be related to the strength of the hydration shell.

When the pressure is raised beyond ~100 MPa, the pressure dependence of the τ_{2R} at 1 °C becomes similar to those at 15 and 30 °C. Actually, at any temperature, in the pressure range higher than 100 MPa, the τ_{2R} values increase with pressure monotonically and the slopes are close to each other within 10% as seen in Figure 1. In the pressure range higher than ~100 MPa, the rotational anomaly of water is vanished, suggesting that the hydration shell is already loose and that the closer packing of the shell slows down the rotation of the solute benzene.

To further clarify the anomalous pressure dependence of the τ_{2R} of benzene in the aqueous solution at 1 °C, we will compare the pressure dependence of the τ_{2R} in the aqueous solution with that in the methanol solution. In methanol, even at the lower temperature of 1 °C, the pressure dependence of the τ_{2R} is similar to that at 30 °C and those for the solvent water at higher temperatures, as shown in Figure 2. According to the comparison of the pressure effects on the rotational mobility of benzene in the aqueous solution and in the methanol solution at different temperatures, the anomalous pressure dependence as seen in the case of the solvent water at a low temperature reflects that the strong hydrophobic hydration shell exists in the pressure range up to 100 MPa in which the benzene molecule can reorient without feeling the effect of the tighter packing.

The pressure dependence of the rotational mobility of the hydration shell water has also been studied for *tert*-butyl alcohol[12] at 8, 30, and 48 °C and for tetrabutylammonium ion[14] at 25 °C by Ueno et al. At any temperature, the rotational correlation time of the shell water around the solutes decreases with pressure and the hydration shell is destroyed by the compression, in contrast to our results in this work. Two reasons may operate to give rise to this apparent disagreement. One is that the temperatures in Veno et al.'s work are rather higher than the temperatures at which an anomalous pressure dependence is observed in this study. The other is that *tert*-butyl alcohol and tetrabutylammonium ion containing hydrophilic moieties involve weaker hydration shells.

5. Pressure Effect on the Hydration Shell

In this section, we will discuss the pressure effect on the hydration shell in terms of the temperature dependences of the activation volumes of the τ_{2R} of benzene, the compressibility of the hydrophobic hydration shell, and the pressure dependences of the activation energies of the τ_{2R} of benzene and water (D_2O). We express the pressure dependence of the τ_{2R} as[27]

$$\frac{\tau_{2R}(p)}{\tau_{2R}(0.1)} = \exp\left\{\frac{(p-0.1)\Delta V^{\ddagger}}{RT}\right\} \quad (4)$$

where p and 0.1 in the parentheses are the pressures in MPa, R is the gas constant, and $\Delta V^{\ddagger}$ is the activation volume in cm^3 mol^{-1}. In the high-temperature range, the plot of the ln τ_{2R} against pressure is almost linear and the slope is proportional to the $\Delta V^{\ddagger}$. At the lower temperatures of 1, 2, and 5 °C, however, the plot of the ln τ_{2R} against pressure is not linear and the $\Delta V^{\ddagger}$ changes with pressure. This result indicates that the structure of the hydrophobic hydration shell is strongly dependent on the pressure at the low temperatures. To compare the $\Delta V^{\ddagger}$ at different temperatures, the $\Delta V^{\ddagger}$ at initial compression is calculated from the slope of a quadratic fit of the ln τ_{2R} against pressure, in which the linear term represents the $\Delta V^{\ddagger}$ at 0.1 MPa. The $\Delta V^{\ddagger}$ is plotted against temperature in Figure 3. The $\Delta V^{\ddagger}$ values for benzene in the aqueous solution at 15 and 30 °C are 3 cm^3 mol^{-1} and much smaller than that for benzene in the methanol solution (6 cm^3 mol^{-1}). This implies that the interaction between benzene and water molecules is very weak and that the hydration shell is rather spherical. At temperatures lower than 15 °C, the $\Delta V^{\ddagger}$ decreases with lowering of the temperature. At 1 °C, the $\Delta V^{\ddagger}$ is close to zero. This means that the hydrophobic hydration shell is strengthened by lowering the temperature and that the rotational mobility of the solute in the shell is not affected by the compression. Concerning the temperature effect at the atmospheric pressure,[2,4] we have shown that the rotational mobility of water molecules in the hydration shell is strongly hindered at lower temperature as mentioned in the previous section. For example, at 0 °C, the τ_{2R} for the shell water is 3 times as large as that for the bulk water, whereas at 30 °C, the τ_{2R} for the shell water is larger than that for the bulk water by only 50%. As mentioned in the previous section, at temperatures lower than 12 °C, the hydrogen bonding effect is superior in the temperature effect to the excluded volume effect on the rotational mobility.[2] In this sense, it is of interest to note that the pressure effect becomes anomalous between 10 and 15 °C.

It has been shown that the rotational dynamics is a sensitive probe to the local molecular environment.[2,3,15−19] We can estimate the strength of the hydration shell against pressure variation through the pressure dependence of the rotational mobility of the solute benzene. In general, it is impossible to relate exactly the pressure dependence of the rotational diffusion coefficient of the solute to the compressibility of the shell. However, when the shell is not compressed rather easily, i.e., the compressibility of the shell water is small, the pressure dependence of the rotational diffusion coefficient will also be small. In this context, we can discuss the compressibility of the hydration shell water through the rotational mobility of the solute benzene. In particular, the anomalous pressure dependence of the τ_{2R} of benzene in the aqueous solution (H_2O) at 1 °C indicates that the compressibility is much smaller than that of pure water (D_2O) up to 100 MPa. Actually, this result is not consistent with other thermodynamic studies. Some authors have measured the compressibility of solutions and estimated the compressibility of the shell water on the basis of the shell model.[28,29] For the solute benzene, the compressibility of the shell water is found to be larger than that of pure water up to 100 MPa and at a higher pressure it is equal to that of pure water. This result indicates that the shell waters are compressed rather easily, in disagreement with our result on τ_{2R}. For alkyl benzene, on the other hand, the compressibility of the shell is smaller up to 100 MPa and at a higher pressure it is equal to that of pure water, in agreement with the pressure dependence of τ_{2R}. In any case, the studies on τ_{2R} and the thermodynamic compressibility suggest that 100 MPa is a transition point from a strong hydration shell to a weak hydration shell. This is consistent with a well-known observation that the anomaly of water is diminished around 100 MPa.

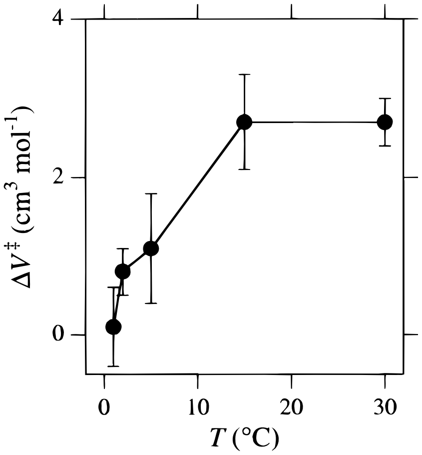

Figure 3. Temperature dependence of the activation volume ($\Delta V^{\ddagger}$) of the rotational correlation times (τ_{2R}) of benzene in the aqueous solution (H_2O).

The difficulty in estimating the excess partial molar compressibility of aqueous solutions is that the shell model is not valid because the excess compressibility strongly oscillates as a function of the shell cutoff distance from the solute benzene.[30] The rotational dynamics probes the hydration shell structure in the vicinity of the solute, while the thermodynamic measurements of the excess compressibility inevitably accounts for the long-range effects. Thus, we believe that the rotational dynamics is a more desirable route to addressing the compression mechanism in the hydration shell.

To reveal the main factor that controls the rotational mobility, we compare the activation energy E_a of the τ_{2R} for benzene and water (D_2O). The activation energy at each pressure was calculated from the linear fitting of ln τ_{2R} against the inverse temperature at 1, 2, 5, 15, and 30 °C. The E_a values of the τ_{2R} for D_2O in pure liquid, benzene in the aqueous solution (H_2O), and benzene in the methanol solution are plotted against pressure in Figure 4. The E_a value for benzene in the aqueous solution decreases with pressure from 15 to 13 kJ/mol. The E_a value for water in pure water also decreases with pressure and reaches a plateau. Thus, the pressure dependence of the E_a of benzene in the aqueous solution is similar to that of water molecules in pure water. In contrast, the activation energy for benzene in methanol increases with pressure as shown in Figure 4. Thus, these two hydrogen bonding solvents have opposite pressure dependences with respect to the activation energy. The behavior observed for benzene in the methanol solution is typical. On the other hand, the peculiarity observed for benzene in the aqueous solution is accounted for by the pressure-induced weakening of hydrogen bonds between water molecules around the solute.

6. Conclusions

We conclude that, at a high temperature, the hydrophobic hydration shell is relatively weak and destroyed easily by compression. In this weak shell, the rotational mobility of a benzene molecule is governed by the packing effect, which is caused by the repulsive interactions between the solute benzene and the solvent water. At a low temperature, a strong hydration shell exists and the compression of the hydration shell is

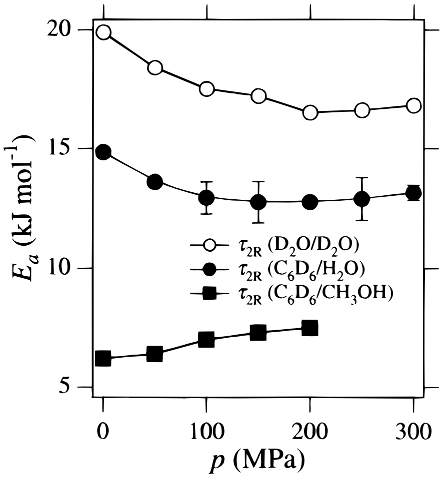

Figure 4. Pressure effect on the activation energies (E_a) of the rotational correlation times (τ_{2R}) of benzene in the aqueous solution (H_2O), heavy water (D_2O) in pure water, and benzene in the methanol solution. When not shown, the error bar is smaller than the size of the symbol. In the symbol X/Y, X and Y denote the solute and the solvent, respectively.

restricted in the pressure range up to 100 MPa. In this strong shell, the rotational mobility of a benzene molecule is not affected significantly by the pressure. When the pressure is raised beyond 100 MPa, the hydration shell is partially destroyed and the rotational mobility is controlled by the packing effect in a manner similar to τ_{2R}'s at high temperatures.

In methanol, there is no strong solvation shell around the solute benzene even at a low temperature and the anomalous pressure dependence is not observed. The τ_{2R} of benzene in methanol increases with pressure through the packing effect in a manner similar to τ_{2R} in the aqueous solution at a high temperature.

The rotational activation volumes $\Delta V^{\ddagger}$ for benzene in the aqueous solution are 3 cm^3 mol^{-1} at 15 and 30 °C and are much smaller than that for benzene in methanol (6 cm^3 mol^{-1}). This implies that the interaction between the benzene and water molecules is rather weak and that the hydration shell is spherical. Especially at 1 °C up to 100 MPa, the $\Delta V^{\ddagger}$ is almost zero. This indicates that the compressibility of the shell is very small, in contrast to thermodynamic measurements of the compressibilities of aqueous solutions.

The rotational activation energy E_a for benzene in the aqueous solution decreases with pressure, and this pressure dependence is similar to that for water in pure water. This result indicates that the rotational activation energy is controlled not by the interaction between the benzene and water molecules but by the hydrogen bonds among water molecules. For benzene in methanol, in contrast, the rotational activation energy increases with pressure.

Acknowledgment. M.N. is grateful for the support of this work by the Research Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture (no. 08230221).

References and Notes

(1) Frank, F., Ed. *Water, A Comprehensive Treatise*; Plenum: New York, 1972−1982; Vols. 1−7.

(2) Nakahara, M.; Wakai, C.; Yoshimoto, Y.; Matubayasi, N. *J. Phys. Chem.* **1996**, *100*, 1345.

(3) Nakahara, M.; Wakai, C.; Matubayasi, N. *J. Phys. Chem.* **1995**, *99*, 1377.

(4) Nakahara, M.; Yoshimoto, Y. *J. Phys. Chem.* **1995**, *99*, 10698.

(5) Fujii, K.; Arata, Y.; Tanaka, H.; Nakahara, M. *J. Phys. Chem. A* **1998**, *102*, 2635.

(6) Laaksonen, A.; Stilbs, P. *Mol. Phys.* **1991**, *74*, 747.

(7) Haselmeier, R.; Holz, M.; Marbach, W.; Weingärtner, H. *J. Phys. Chem.* **1995**, *99*, 2243.

(8) Holz, M.; Haselmeier, R. K.; Mazitov, H.; Weingärtner, H. *J. Am. Chem. Soc.* **1994**, *116*, 801.

(9) Weingärtner, H.; Haselmeier, R.; Holz, M. *Chem. Phys. Lett.* **1992**, *195*, 596.

(10) Jonas, J.; DeFries, T.; Wilbur, D. J. *J. Chem. Phys.* **1976**, *65*, 582.

(11) Hertz, H. G.; Zeidler, M. D. *Ber. Bunsen-Ges. Phys. Chem.* **1964**, *68*, 821.

(12) Yoshida, K.; Ibuki, K.; Ueno, M. *J. Chem. Phys.* **1998**, *108*, 1360.

(13) (a) Bradl, S.; Lang, E. W. *J. Phys. Chem.* **1993**, *97*, 10463. (b) Bradl, S.; Lang, E. W.; Turner, J. Z.; Soper, A. K. *J. Phys. Chem.* **1994**, *98*, 8161.

(14) Ueno, M.; Tsuchihashi, N.; Yoshida, K.; Ibuki, K. *J. Chem. Phys.* **1996**, *105*, 3662.

(15) Nakahara, M.; Wakai, C. *J. Chem. Phys.* **1992**, *97*, 4413.

(16) Matubayasi, N.; Nakahara, M. *J. Chem. Phys.* **1991**, *94*, 653.

(17) Wakai, C.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 853.

(18) Wakai, C.; Nakahara, M. *J. Chem. Phys.* **1994**, *100*, 8347.

(19) Wakai, C.; Nakahara, M. *J. Chem. Phys.* **1995**, *103*, 2025.

(20) IUPAC. *Solubility Data Series, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5-C_7*; Shaw, D. G., Ed.; Pergamon: London, 1989; Vol. 47, p 63.

(21) Nakahara, M. *Rev. High-Pressure Sci. Technol.* (in Japanese) **1992**, *1*, 195.

(22) Woolf, L. A. *J. Chem. Soc., Faraday 1* **1976**, *72*, 1267.

(23) Gaballa, G. A.; Neilson, G. W. *Mol. Phys.* **1983**, *50*, 97.

(24) Matubayasi, N. *J. Am. Chem. Soc.* **1994**, *116*, 1450.

(25) (a) Assael, M. J.; Papadaki, M.; Wakeham, W. A. *Int. J. Thermophys.* **1991**, *12*, 449. (b) Collings, A. F.; McLaughlin, E. *Trans. Faraday Soc.* **1971**, *67*, 340.

(26) Isdale, J. D.; Easteal, A. J.; Woolf, L. A. *Int. J. Thermophys.* **1985**, *6*, 439.

(27) Zwanzig, R.; Harrison, A. K. *J. Chem. Phys.* **1985**, *83*, 5861.

(28) Sawamura, S.; Kitamura, K.; Taniguchi, Y. *J. Phys. Chem.* **1989**, *93*, 4931.

(29) Chalikian, T. V.; Sarvazyan, A. P.; Breslauer, K. J. *Biophys. Chem.* **1994**, *51*, 89.

(30) Matubayasi, N.; Levy, R. M. *J. Phys. Chem.* **1996**, *100*, 2681.