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ARTICLES

Pressure and Temperature Effects on the Hydrogen-Bond Structures of Liquid and Supercritical Fluid Methanol

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The proton spin−lattice relaxation times and proton chemical shifts for the hydroxyl and methyl protons in methanol were measured at liquid and supercritical densities using capillary high-pressure NMR spectroscopy. The pressure range for the proton nuclear relaxation measurements was between 50 and 3500 bar over a temperature range of 298−573 K. The proton chemical shifts of methanol were investigated for a pressure range of 50−3500 bar and a temperature range of 298−773 K. Attempts were made to separate the contributions of the dipolar and spin−rotation interactions to the spin-relaxation processes at each thermodynamic condition over methanol densities ranging from liquid to supercritical fluid. An average number of hydrogen bonds per molecule in methanol and the apparent activation energy of the methyl group internal rotation have been extracted from the experimental relaxation data. The extracted quantities show a moderate pressure dependence in addition to temperature effects, which suggest that molecular packing effects on hydrogen-bonded methanol are important at higher pressures. A comparison between methanol and water at similar thermodynamic conditions was also made to obtain new insight into these two important supercritical solvents.

Introduction

Methanol, the simplest alcohol, provides an ideal model compound to investigate the pressure and temperature dependence of hydrogen bonding. Although in many ways similar to supercritical water, for a reaction and separation solvent, methanol is far less corrosive and aggressive in nature. The understanding of intermolecular interactions in such a solvent at supercritical conditions has become important.[1] Various spectroscopic studies, such as NMR,[2,3] IR,[4−6] Raman,[7] X-ray,[8] neutron diffraction,[9] and dielectric measurement,[10] have been performed on liquid methanol. Theoretical molecular simulation studies[11,12] on hydrogen-bonding structures in methanol have been reported. Using pressure as a thermodynamic variable, high-pressure NMR spectroscopy is found to be an effective means of exploring the hydrogen bonding in methanol. High-pressure NMR investigations of methanol include proton chemical shift,[13,14] self-diffusion coefficient,[15,16] and spin−lattice relaxation measurements.[17,18]

Schulman et al.[15] investigated the difference in the proton chemical shift between the CH_3 and OH groups of methanol from 278 to 392 K at pressures up to 1000 bar. Our previous chemical shift measurements[16] covered a temperature range of 297−413 K and a pressure range of 500−2600 bar. Recently, Hoffmann and Conradi[17] reported proton chemical shift data of methanol as a function of temperature (323 and 723 K) and pressure (1−350 bar). They noted that hydrogen-bonding interactions in methanol continue to play an important role even at the highest temperatures in their study. The self-diffusion coefficients of deuterated methanol have been measured for a temperature range of 223−323K up to 4900 bar by Jonas and Akai.[18] Karger et al.[20] extended the self-diffusion measurements of methanol to a temperature range between 150 and 450 K and to pressures up to 2500 bar using a NMR spin−echo technique with pulsed field gradients. It is found that the translational mobility in methanol is dominated by the intermolecular anisotropic interactions, such as hydrogen bonding.[20] Unlike the proton chemical shift and self-diffusion measurements, the nuclear spin−lattice relaxation time (T_1) measurements for methanol at high pressure are surprisingly scarce, although numerous investigations have been performed under ambient pressure.[19,20] The ^{13}C spin−lattice relaxation rates and nuclear Overhauser effect (NOE) in methanol have been measured for CO_2−methanol mixtures at binary supercritical conditions.[21,22] Methanol hydrogen-bonding structures were found to be significant, even in dilute CO_2 solutions. Recent developments in high-pressure NMR studies of hydrogen-bonded liquids may be found in a review article by Lang and Lüdemann.[21]

Nuclear magnetic resonance measurements including chemical shift and spin−lattice relaxation offer experimental data from which the degree of hydrogen bonding, the number of hydrogen bonds per molecule, and the internal rotation rate of the methyl group may be extracted. The measurement of the strength and extent of hydrogen bonding in methanol under various thermodynamic conditions is critical in understanding the solution structure of methanol. Changes in the proton chemical shift

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difference between the CH_3 and OH groups provide a measure of the degree of hydrogen bonding in methanol. The number of hydrogen bonds per molecule is another important parameter that allows a direct comparison between experiment and molecular simulation under similar thermodynamic conditions.

In this paper, proton spin−lattice relaxation times (T_1) were measured for the first time for the hydroxyl and methyl protons as a function of temperature and pressure up to 3500 bar and 573 K. In addition, the $^{13}C-\{^1H\}$ NOE effects and deuterium relaxation rates in methanol were also measured at selected temperatures and pressures. The spin−lattice relaxation data, which depend on fluctuations in molecular reorientational motions as a consequence of molecular collisions, provide valuable information about the nature and average rate of molecular motion in both liquid and supercritical methanol. The deuterium T_1 and NOE measurements enable us to separate relaxation mechanisms and to estimate inter- and intra- molecular interaction contributions in methanol over various thermodynamic conditions. The average number of hydrogen bonds per molecule as a function of temperature was obtained based on the experimental relaxation data and a phenomenological model of the hydrogen bond network in methanol. These results agree qualitatively with molecular dynamic simulations at similar thermodynamic conditions. The methyl group's internal rotational activation energy is estimated from experimental proton relaxation rates. The temperature dependence of the average hydrogen-bond number and activation energy is also discussed. Proton chemical shift measurements of methanol have been extended over a temperature range of 298−773 K and a pressure range of 50−3500 bar. The measurement of the spin−lattice relaxation time, which complements the chemical shift measurement, provides valuable physicochemical information on hydrogen bonding in methanol.

Experimental Section

Anhydrous methanol (Aldrich Chemical Co., Inc.) was further degassed using a standard freeze−pump−thaw procedure. Deuterated methanol (Cambridge Isotope Laboratories) and ^{13}C-labeled methanol (Aldrich) were used without further purification. All NMR data were obtained on a Chemagnetics CMX300 NMR spectrometer operating at 298.3 MHz for the proton frequency. A high-temperature, high-resolution, broad-band 10-mm NMR probe (Doty Scientific, Inc.) was used in the measurements. A line width at half-height of 4−8 Hz was obtained for the methyl-group protons over all temperatures and pressures studied. The probe temperature was calibrated using a reference thermocouple. The relative reproducibility in the temperature measurement is estimated to be about ±2 K for low (<550 K) and ±5 K for high (>550 K) temperatures. The capillary high-pressure NMR cell utilized in this study has been described previously.[22,23] The fused silica capillary tubing (100 μm i.d. and 360 μm o.d., Polymicro Technologies, Inc.) was flame sealed, evacuated, and then filled with degassed methanol. This fused silica capillary NMR cell produces a sufficient sensitivity with four scans, even at the highest temperatures used. The sample pressure was measured using a calibrated pressure transducer (Precise Sensors, Inc.) with a precision of ±0.7 bar. A standard inversion recovery pulse sequence[24] ($10T_1$-$\pi-\tau$-$\pi/2$) was used to measure the spin−lattice relaxation times, and the reproducibility of T_1 is about 5% and 8% for the methyl and hydroxyl groups, respectively, for both proton and deuterium relaxation measurements. The measured magnitude of the NOE, defined by the ratio of the integrated intensity of a proton-decoupled ^{13}C spectrum to that of the equilibrium intensity of a coupled spectrum,[29] has a relative accuracy of ±8%. The reproducibility of the proton chemical shift measurements is estimated to be ±0.05 ppm.

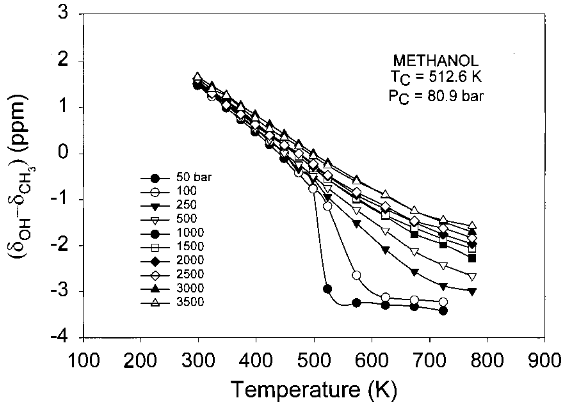

Figure 1. Differential chemical shifts of the hydroxyl and methyl protons in methanol as a function of pressure and temperature.

With a standard 5-mm glass tube at ambient pressure, the hydroxyl and methyl proton T_1's for degassed methanol were determined to be 5.5 and 6.9 s, respectively. Using a capillary cell, T_1's were found to be 5.1 and 6.7 s for the hydroxyl and methyl protons, respectively, at room temperature and pressure. The T_1 values obtained with a 5-mm glass tube and the capillary tube are comparable within experimental error, indicating that a reliable T_1 measurement can be expected from a capillary high-pressure NMR cell.

Results and Discussion

Proton Chemical Shift. The proton chemical shift difference between the hydroxyl and methyl groups of methanol is known to be a strong function of temperature.[2] The pressure effects on this difference have also been investigated over various pressure ranges.[15−17] The chemical shift measurements for pure methanol were extended in this study to a temperature range from 298 to 773 K and for pressures up to 3500 bar. The isobaric measurements are shown in Figure 1 as a function of temperature. A dramatic change of the chemical shift difference in the vicinity of the methanol critical point is observed. This change is related to the large changes in density and hydrogen bonding in this region. Proton chemical shift differences in methanol as a function of temperature and pressure have been discussed[15−17] previously and will not be repeated here. A linear temperature dependence of the chemical shift difference was observed in Figure 1 at temperatures less than 600 K and at pressures greater than 1000 bar. Deviations from this linear dependence were noted at temperatures higher than 600 K. At higher pressures, it appears that more thermal energy is needed to disrupt the hydrogen bonding in methanol. A complete explanation for this observation is not entirely clear at present. However, the chemical shift data presented in Figure 1 clearly indicate that significant hydrogen-bond interactions exist for methanol at high temperatures and pressures.

The chemical shift data of Hoffmann and Conradi[17] was compared with earlier measurements[2,3,16] at comparable temperatures and pressures, in which excellent agreement was noted. The results reported here using the capillary high-pressure cell are in good agreement with those of Hoffmann and Conradi over their temperature and pressure range.

Proton Spin−lattice Relaxation Time. Proton T_1 isotherms between 298 and 573 K have been measured for the hydroxyl and methyl protons up to 3500 bar; the results are presented in

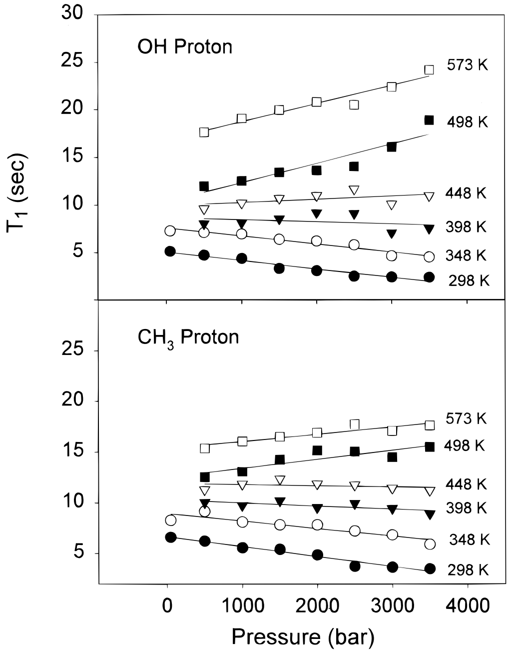

Figure 2. Isothermal proton spin−lattice relaxation times of the hydroxyl and methyl groups in methanol as a function of pressure.

Figure 2. It is interesting to note that T_1 values decrease slowly as the pressure increases at lower temperatures (<448 K), however, T_1 values increase as a function of pressure at higher temperatures (>498 K). If dipole−dipole (DD) interactions dominate the relaxation process, then the spin−lattice relaxation time decreases with increasing pressure at constant temperature. As sample pressure increases, the viscosity increases and the self-diffusion coefficient decreases, which leads to an increase in the molecular reorientational correlation time and a reduction in the relaxation time. This is observed at lower temperatures (<398 K).

Spin−rotation interactions are modulated by changes in the molecular angular momentum due to molecular collisions. At higher temperatures (>498 K), the proton relaxation process is dominated by spin−rotation (SR) interactions because the proton relaxation time increases with pressure. As pressure increases at a constant temperature, density increases and the molecular collisional frequency increases, leading to a decrease in the molecular angular momentum exchange correlation time, τ_J. Therefore, the spin−rotation relaxation time increases with decreasing τ_J. The data shown in Figure 2 indicates that the dominant nuclear spin relaxation mechanism in methanol changes with temperature. The SR and DD interactions dominate the proton relaxation mechanism at high and low temperatures, respectively. This relaxation mechanism change with temperature becomes obvious as pressure is used as a variable in the measurement.

Methanol has a critical temperature of 512.6 K;[25] the relaxation process appears to be dominated by the spin−rotation relaxation mechanism near this temperature. To further verify the change in mechanism, the ^{13}C−{^{1}H} NOE effect was measured at 1000 bar as a function of temperature, and the results are shown in Figure 3. As noted in the figure, the NOE enhancement decreases with temperature and approaches unity; which is the SR interaction limit if no other random molecular motion competes at high temperatures.[29] It is understood that the NOE data reveal only the significant mechanisms for the ^{13}C nuclear relaxation. However, they are related to the proton relaxation since the ^{1}H and ^{13}C nuclei are strongly coupled in a small molecule like methanol.

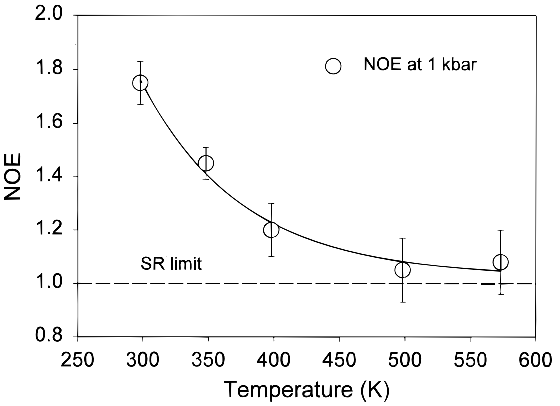

Figure 3. ^{13}C−{^{1}H} NOE in methanol as a function of temperature at 1000 bar. The dashed line represents the SR limit, assuming that no other random motions contribute to spin relaxation other than SR interactions.

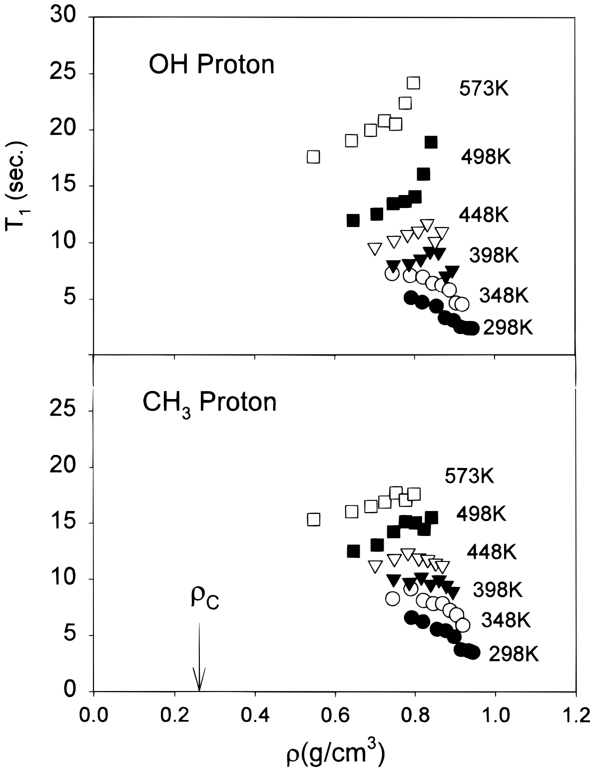

Figure 4. Density dependence of the proton spin−lattice relaxation time for the hydroxyl and methyl protons in methanol at various isotherms.

In the investigation of liquid and supercritical water using proton relaxation measurements, Jonas et al.[26,27] found that dipolar interactions dominate the relaxation process at low temperatures ($T \leq 500$ K); this interaction becomes less important at higher temperatures. Near or above the critical temperature of water, the spin−rotation interaction dominates proton relaxation and T_1 shows a linear dependence on density up to 1.5ρ_C, where ρ_C is the critical density of water. The density dependence of the isothermal proton relaxation times for the hydroxyl and methyl protons in methanol is shown in Figure 4. Methanol densities were interpolated from the thermodynamic tables at the temperatures and pressures investigated.[28] At low temperatures, the proton relaxation time of methanol decreases with increasing methanol density. The inverted density dependence of the relaxation time is noted at high temperatures, due to a change in proton spin-relaxation mechanisms in methanol. Although our measurements did not cover densities lower than 0.65 g/cm^3, a similar T_1 density dependence is noted for methanol as compared with that for water reported by Jonas et al.[31,32] at comparable reduced densities. The larger uncertainty (±8%) in the hydroxyl proton relaxation data, especially at high temperatures, is due to the signal intensity of the hydroxyl proton being 3 times smaller than that of the methyl protons. Therefore, a larger error is anticipated in the relaxation data for the hydroxyl protons.

Spin-Relaxation Mechanism in Methanol. The possible relaxation mechanisms for protons in methanol under our experimental conditions are dipolar, spin−rotation, chemical shift anisotropy (CSA), and scalar coupling (SC). The CSA contribution to the proton relaxation rate is estimated to be less than 10^{-5} s^{-1} in methanol.[24] Scalar coupling depends on the proton exchange rate and is important at exchange rates intermediate between pure and highly acidified methanol.[29,30] For pure methanol, the contribution of scalar coupling to the relaxation rate of the hydroxyl proton, $[T_1(\mathrm{OH})]_{\mathrm{SC}}^{-1}$, was estimated to be 1.2×10^{-3} s^{-1}, which is less than 3% of the total experimental relaxation rate at room temperature.[24] The exchange correlation time increases rapidly with an increase of temperature due to a reduction in methanol density. The SC coupling becomes less important at high temperatures. Therefore, the total experimental relaxation rate, $1/T_1$, may be expressed as the summation of contributions from dipolar coupling $(1/T_1)_{\mathrm{DD}}$ and spin−rotation coupling $(1/T_1)_{\mathrm{SR}}$. The term $(1/T_1)_{\mathrm{DD}}$ may be further divided into contributions from intermolecular and intramolecular interactions.

The relaxation data of liquid and supercritical water from Jonas et al.[31,32] suggest that a gas kinetic spin−rotation relaxation theory may be used to interpret the experimental spin-relaxation data at high temperatures and low densities. If methanol is approximated as a symmetrical top molecule with one internal degree of freedom associated with rotation of the methyl group about its 3-fold axis, the SR coupling may be expressed as[22,31]

$$R_1^{\mathrm{SR}} = (2\pi^2/\alpha)C_{\mathrm{eff}}^{\ 2}\tau_{\mathrm{J}} \tag{1}$$

where $\alpha = \hbar^2/(2kTI_\perp)$ and $I_\perp$ (0.658×10^{-46} Kg m^2) is the perpendicular component of the moment of inertia. The effective spin−rotation constant, C_{eff}, for the proton in the hydroxyl group was found to be 9.9 kHz.[24] According to the gas kinetic theory, τ_{J}, the effective spin−rotation correlation time, may be expressed as a function of fluid density (ρ) and the average molecular velocity ($\tilde{v}$): $\tau_{\mathrm{J}} = 1/(\rho\tilde{v}\sigma_{\mathrm{K}})$[32] where $\sigma_{\mathrm{K}} = \pi d^2$,[33] the kinetic collisional cross-section, may be calculated by assuming d is treated as the Lennard−Jones distance parameter (0.363 nm for methanol).[30] In this treatment, the effective spin−rotation correlation time, τ_{J}, is linearly proportional to the kinetic collisional time between molecular collisions and an assumption is made that on average only one collision is needed for an effective molecular angular momentum exchange. In principle, the spin−rotation relaxation rates of methanol may be estimated using eq 1 if reliable density data are available.

The contribution to spin−lattice relaxation from intermolecular dipolar interactions are modulated by molecular translational diffusion. If reliable self-diffusion coefficients, D, are available, this contribution may also be estimated as[34]

$$R_1^{\mathrm{inter}} = \frac{2\pi}{15}\frac{N\gamma^4\hbar^2}{aD} \tag{2}$$

where N is the proton number density and a is the distance of closest approach between hydrogens. For hydroxyl−hydroxyl intermolecular interactions, a is generally taken to be $1.2r$, where r is the molecular radius of methanol, having a value of 0.229 nm.[24] The intramolecular dipolar contribution to the total relaxation rate is closely related to molecular tumbling motions, represented by the molecular reorientational correlation time, τ_{C}[39]

$$R_1^{\mathrm{intra}} = \frac{3}{2}\hbar^2\gamma^4\left(\sum_{i\neq j}\frac{1}{r_{ij}^{\ 6}}\right)\tau_C \tag{3}$$

where r_{ij} is the internuclear distance. A scaled model[24] of methanol chain and ring structures were used to obtain the H−H distance. For chain structures, the nearest-neighbor hydrogens have a distance of 0.23 nm, $r_{\mathrm{H-H}}$, and the next set of hydrogens a distance of 0.43 nm. Therefore, an effective distance of 0.229 nm ($(0.23^{-6} + 0.43^{-6})^{-1/6}$) is obtained. Because of strained structures, the cyclic dimer and trimer are considered to be present in very small concentrations, if they exist at all. With an increase in ring size to pentamers, hexamers, or larger rings, the $r_{\mathrm{H-H}}$ distance becomes nearly the same as in the chain structures. Therefore, large rings are indistinguishable from chain structures in terms of H−H distance. In this model, methanol is a mixture of chains and cyclic tetramers, where chains are considered as containing both linear polymers of varying size and large ring structures. In such a scaled hydrogen-bond model, the summation in eq 3 can be written in an average form[35]

$$\sum_{i\neq j}\frac{1}{r_{ij}^{\ 6}} = \frac{\langle n_{\mathrm{HB}}\rangle}{\langle r_{ij}\rangle^6} \tag{4}$$

where $\langle n_{\mathrm{HB}}\rangle = (2(n-1)/n)$ is the average number of neighboring molecules in the vicinity of the methanol of interest, which is equivalent to the average number of hydrogen bonds per molecule. n is the average aggregation number of methanol in the hydrogen-bonded fluid. A range of $\langle n_{\mathrm{HB}}\rangle$ between 0 and 2 relates to an average aggregation number in methanol of $n = 1$ to ∞.

For methanol, an alternative way to determine τ_{C} is to measure the deuterium spin−lattice relaxation time of CD_3OD. In this case, spin−lattice relaxation is dominated by quadrupolar effects which are modulated by the molecular motion similar to intramolecular dipolar coupling present in the extreme narrowing case.[26] For a deuterium nucleus (spin = 1), quadrupole relaxation may be expressed as[39]

$$R_1^{\mathrm{Q}} = \frac{3}{8}(1 + \eta^3/3)(eQ/\hbar)^2\tau_C \tag{5}$$

In eq 5, η is the asymmetry parameter of the gradient of the electric field strength at the ^{2}H nucleus. A theoretical calculation[36] showed the asymmetry parameter η was less than 0.152, so that the factor $(1 + \eta^3/3)$ may be neglected. The quadrupole coupling constant, $eQ/\hbar$, has been reported to be 210 kHz for the ^{2}H nuclei in the OD group in methanol.[37,38] If it is assumed that $eQ/\hbar$ is constant over the temperature ranges studied, eq 5 provides a way of estimating the molecular reorientational correlation times for the hydroxyl group in methanol if the experimental deuterated relaxation rates are available.

Spin Relaxation−Hydroxyl Group. The pressure-averaged (50−3500 bar) experimental proton relaxation rates for the OH group is shown in Figure 5, with the standard deviations

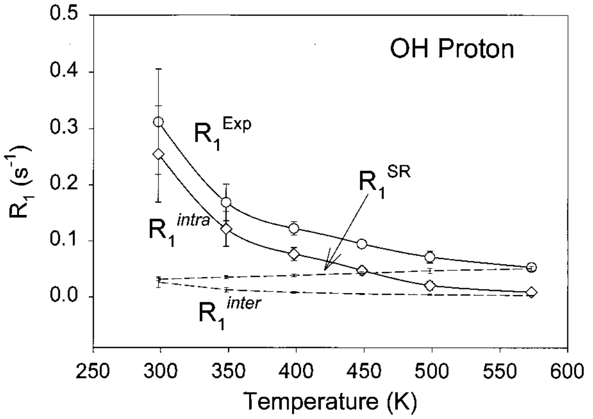

Figure 5. Separation of the hydroxyl proton relaxation mechanisms based on the experimental methanol density[33] and self-diffusion coefficient data[20] using eqs 1 and 2.

TABLE 1: Deuterium Spin−Lattice Relaxation Times, $T_1(^2H)$, for the OD Group in CD_3OD

	$T_1(^2H)$ (s) pressure (bar)				
temp (K)	100	500	1000	$\bar{T}_1(^2H)$ (s)	τ_C (ps)
298	0.21	0.18	0.23	0.21	26
348	0.34	0.37	0.31	0.34	16
398	0.39	0.41	0.42	0.41	13

represented as the error bars. Using eq 1, the spin−rotation coupling contribution to the proton relaxation rate in the hydroxyl group has been calculated based on the methanol density.[33] The pressure-averaged (50−3500 bar) spin−rotation relaxation rate as a function of temperature is also presented in Figure 5, along with the error bars representing the standard deviations over the pressure range. The pressure-averaged relaxation rates were used in Figure 5 because even though temperature plays a major role in changes in the spin−lattice relaxation mechanism, pressure appears to have a minor effect at lower temperatures.

Using the measurements of the self-diffusion coefficients of methanol at high temperature and pressure as reported by Karger et al.,[21] we are able to estimate the contributions due to intermolecular dipole−dipole interactions with eq 2, which are presented in Figure 5. The intramolecular interaction contribution shown in Figure 5 was obtained by subtracting the spin−rotation and the intermolecular dipolar contributions from the total experimental relaxation rate. According to gas kinetic theory, the spin−rotation relaxation mechanism gradually becomes important in the proton relaxation process of the OH group in methanol with an increase of temperature and eventually appears to dominate the relaxation process at temperatures greater than 500 K. It is noted that the intermolecular interaction plays a minor role in the proton relaxation of the OH group in methanol under our experimental conditions. It remains small and constant over the temperature range studied. The intramolecular dipolar coupling follows the same trend as the total experimental relaxation rate as a function of temperature, except its contribution appears to vanish at high temperatures. It can be seen from Figure 5 that intramolecular dipolar interactions dominate proton relaxation at lower temperatures (300−400K), while spin−rotation interactions dominate at higher temperatures (>500K). The dipolar and spin−rotation interactions compete with each other at temperatures between 400 and 500 K.

The molecular reorientational correlation times, τ_C, of the OH group in methanol may be estimated using the deuterium spin−lattice relaxation times, $T_1(^2H)$, in CD_3OD due to quadrupolar relaxation. The values for $T_1(^2H)$ measured at 298, 348 and 398 K up to 1000 bar are presented in Table 1. The measured $T_1(^2H)$ depends on temperature but remains constant with pressure within experimental error, which allows us to calculate a pressure-averaged value. Table 1 lists the average $T_1(^2H)$ values, from which the molecular reorientational correlation times, τ_C, may be calculated using eq 5. The values for τ_C range from 13 to 26 ps over the temperature range studied. Assuming that the reorientational correlation time determined from quadrupole relaxation rates is similar to the *intra*molecular spin relaxation, then the average number of hydrogen bonds per molecule $\langle n_{HB} \rangle$ may be obtained by solving eqs 3 and 4.

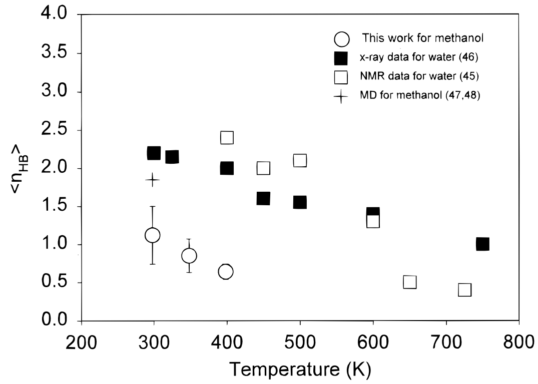

Figure 6. Average number of hydrogen bonds per molecule in methanol and water versus temperature.

For visual clarity, the pressure-averaged $\langle n_{HB} \rangle$ from the spin−lattice relaxation measurements is shown in Figure 6 as a function of temperature. No attempts were made to estimate the average $\langle n_{HB} \rangle$ at higher temperatures (>400 K) because the intramolecular relaxation mechanism no longer dominates the relaxation process at these temperatures. The values of $\langle n_{HB} \rangle$ for water[39] have been determined from high-pressure NMR[40] and X-ray spectroscopy.[41] These data are also plotted in Figure 6. It is noted that $\langle n_{HB} \rangle$ of methanol has a similar trend to that of water; they both decrease with an increase of temperature. The maximum value of $\langle n_{HB} \rangle$ is 2 and 4 for solid methanol and ice-I, respectively.[44] It is seen in Figure 6 that both water and methanol are at ~50% of their maximum $\langle n_{HB} \rangle$ at room temperature and decrease as a function of temperature, eventually approaching zero, the monomer limit. It is necessary to mention that $\langle n_{HB} \rangle$ for methanol obtained in this study strongly depends on the choice of model and on the assumptions made. The calculation of $\langle n_{HB} \rangle$ appears to produce a correct trend of $\langle n_{HB} \rangle$ for methanol as a function of temperature. Molecular dynamic simulations for liquid methanol at room temperature suggest each molecule forms 1.85 hydrogen bonds,[42,43] which does not agree with our quantitative result (1.12 hydrogen bonds) at room temperature. The overall trend in Figure 6 qualitatively agrees with the methanol cluster distribution determined using molecular dynamic (MD) simulations.[17] An increase in temperature does not favor the formation of large hydrogen-bonded clusters, and therefore, $\langle n_{HB} \rangle$ decreases.

Spin Relaxation−Methyl Group. Using a similar procedure as that described in the previous sections, the intramolecular relaxation rates for the methyl-group protons may be separated from the total experimental relaxation rates. For the methyl-group protons, the internuclear distance, r_{HH}, is 0.178 nm[40] which should be independent of the hydrogen-bond network. Equation 3 can be simplified as

$$R_1^{\text{intra}} = \frac{3}{2}(n-1)\hbar^2\gamma^4\frac{1}{r_{\text{HH}}}\tau_C \tag{3′}$$

where n is the number of methyl protons in the molecule. Therefore, the molecular reorientational correlation time τ_C as a function of temperature and pressure may be extracted from the experimental proton relaxation rate. The reorientational correlation time obtained in this manner may be related to a methyl group's internal rotational diffusion, assuming methyl internal rotation is much faster than the overall molecular tumbling for methanol. If the rotational molecular motion is thermally activated, the effective internal rotation activation energy, E_a, may be obtained from the temperature dependence of the reorientational correlation time at constant pressure[26]

$$\tau_C = \tau_0 \exp(E_a/RT) \tag{6}$$

Figure 7 shows a linear dependence of τ_C versus $1/T$ for the methyl-group relaxation over a temperature range of 298−498 K at 500 and 3500 bar. The correlation time data of other pressures studied are not plotted in the figure for clarity but showed a similar linear behavior. τ_0 in eq 6 is the reorientational correlation time at the high-temperature, low-density limit and it is determined to be 0.02 ± 0.01 ps for the methyl group internal rotation from Figure 7. The intercept value of 0.02 ps is an average value for the pressure range in this study. This correlation time is compared with the free-rotor correlation time using a gas kinetic theory, which may be expressed as[44]

$$\tau_{\text{free-rotor}} = \frac{2\pi}{9}\left(\frac{I_\perp}{kT}\right)^{1/2} \tag{7}$$

where $I_\perp$ is the perpendicular component of the moment of inertia for methanol. Using eq 7, the free-rotor correlation time for methanol is 0.06−0.08 ps over the temperature range of 300−500K. The two correlation times are comparable, which lends credence to the activation energies determined from the slope in Figure 7.

The apparent activation energies for the methyl group's internal rotation are plotted in Figure 8 as a function of pressure. The internal rotation potential-energy barrier of methanol at ambient pressure[45] is also given in Figure 8. The activation energy gradually increases with increasing pressure but levels off above 2500 bar, indicating that internal rotation of the methyl group may be affected by molecular packing due to the pressure effect on the molecular free volume. Pressure effects on molecular internal rotation have been observed previously for *tert*-butyl alcohol. An apparent activation energy of 3.4 kcal/mol for the *tert*-butyl group in *tert*-butyl alcohol at ambient pressure[46] increases to 5.0 ± 0.2 kcal/mol at a pressure range of 100−1000 bar.[47] It is anticipated that the activation energy of internal rotation in methanol would be smaller than that in *tert*-butyl alcohol, even at the highest pressure in this study, because of a smaller energy barrier for internal rotation in the methyl group as compared to that in *tert*-butyl alcohol.

Conclusions

The difference in chemical shifts between the hydroxyl- and methyl-group protons as a function of temperature and pressure show a significant change in hydrogen bonding near the critical point of methanol, but hydrogen bonding is still extant under these conditions. These measurements ($\delta_{\text{OH}} - \delta_{\text{CH}_3}$)) have been extended to a pressure range of 3500 bar. In general, an enhancement in the hydrogen-bonding network of methanol is seen with increasing pressure at constant temperature and hydrogen-bonding decreases with increasing temperature at constant pressure. This is similar to our earlier reported molecular dynamics simulations of methanol.[16]

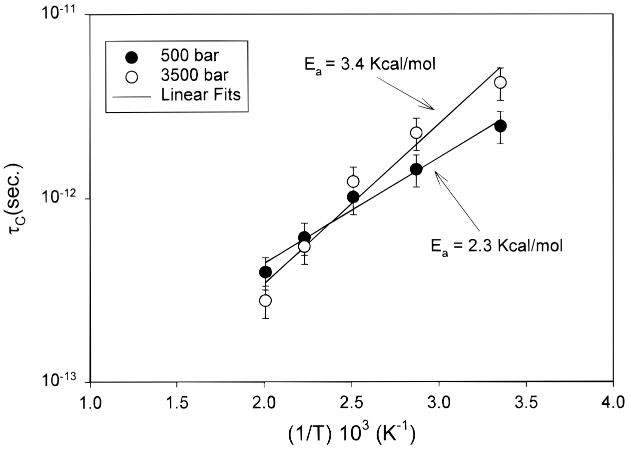

Figure 7. Linear dependence of τ_C versus $1/T$ at 500 bar (●) and 3500 bar (○), respectively. Solid lines are linear least-squares fit to the data.

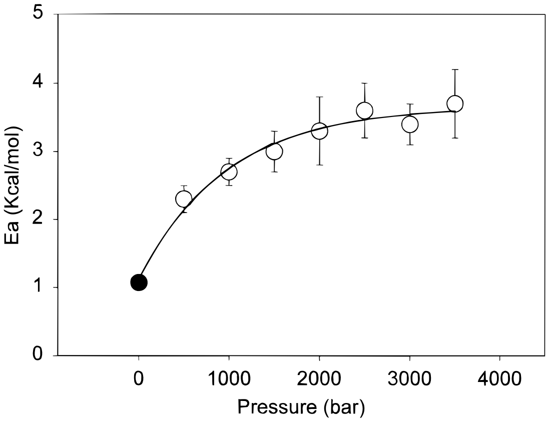

Figure 8. Apparent activation energy of the internal rotation of the methyl group as a function of pressure. Open circles (○) represent data of this study, and the filled circle (●) represents data from ref 50. The solid line is used to connect the experimental points for visual clarity.

Spin−lattice relaxation measurements provide valuable dynamic information, such as reorientational correlation times for both the methyl and hydroxyl groups, which enhances our understanding of the hydrogen-bond network in liquid and supercritical methanol. The reorientational correlation time of the methyl internal rotation is thermally activated, and the activation energies were determined as a function of pressure. The activation energy increases slowly with increasing pressure and levels off above 2500 bar, indicating that pressure affects molecular packing in methanol. Overall, as anticipated, the activation energy of internal rotation for the methyl group in methanol is less than the internal rotational barrier of the *tert*-butyl group in *tert*-butyl alcohol.

The average number of hydrogen bonds per molecule in methanol, as determined from the experimental relaxation rates, decreases with increasing temperature, which is consistent with the results from proton chemical shift measurements ($\delta_{\text{OH}} - \delta_{\text{CH}_3}$) and our previous molecular dynamic simulations. Not surprisingly, water and methanol share many similarities with respect to their hydrogen-bond structure and molecular dynamics over a large range of temperatures and pressures.

Finally, the attempts made in separating the mechanisms of spin−lattice relaxation from our measurements lead one to the following conclusions. Dipolar interactions dominate proton spin relaxation in methanol over a temperature range from 300 to 400 K, and the spin–rotation interaction is the major relaxation mechanism at temperatures above 500 K. The two relaxation mechanisms compete with each other over a temperature range of 400–500 K.

These conclusions lead us to postulate a physical model for methanol in which methanol is composed of linear hydrogen-bonded chains. The average length of these chains decreases with increasing temperature, and pressure apparently increases the average chain length. This is consistent with both molecular dynamics simulations and chemical shift measurements ($\delta_{OH} - \delta_{CH_3}$) for methanol. In a similar manner, the increase in activation energy for the internal rotation of the methyl group with pressure is related to the packing density of these chains. As methanol is compressed, this apparently hinders the free rotation of the methyl groups in these linear structures, but a stable compressed structure is achieved as the activation energy approaches a constant value at high pressures.

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