NMR Studies on Effects of Temperature, Pressure, and Fluorination on Structures and Dynamics of Alcohols in Liquid and Supercritical States

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We measured ^{1}H NMR chemical shifts (δ_H) and ^{1}H and ^{2}H NMR spin−lattice relaxation times (^{1}H- and ^{2}H-T_1) of methanol, ethanol, 2-propanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol in the temperature range from 298 to 673 K at reduced pressures ($P_r = P/P_c$) of 1.22 and 3.14. The δ_H values showed that the degree (X_{HB}) of hydrogen bonding decreased in the order of methanol > ethanol >2-propanol > H_2O, and that the hydrogen bonding was much affected by fluorination, because of the intramolecular H−F interactions in supercritical (sc) states. Moreover, ^{1}H-T_1 measurements revealed that the relaxation processes of OH groups in nonfluoroalcohols are controlled by dipole−dipole (DD) and spin–rotation (SR) mechanisms below and above the critical temperature (T_c), while the cross-correlation effects connected with intramolecular DD interactions between a carbon atom and an adjacent proton played an important role for hydrocarbon groups (CH_n, $n = 1-3$) under sc conditions. This interpretation was also supported by two other results. The first is that the intramolecular H−F interactions strongly inhibit the internal rotation of CH and CH_2 groups of sc fluoroalcohols, and the second is that the molecular reorientational correlation times (τ_c^D) obtained from ^{2}H-T_1 values of deuterated hydrocarbon groups (CD_n) at temperatures above T_c have significantly less temperature dependence than those of OD groups. Actually, the apparent activation energy (ΔE_a) for molecular reorientational motions in sc alcohols was smaller compared with liquid alcohols, being about 1 order of magnitude.

Introduction

Supercritical (sc) fluids have been paid much attention as environmentally benign media in various fields of chemistry and engineering, because of their density-tunable physicochemical properties.[1,2] By utilizing sc carbon dioxide ($scCO_2$) and/or sc water (scw), complicated chemical processes have been realized such as syntheses of organic substances, extractions and separations of metal complexes and chelating ligands from materials, and hydrolysis treatment of hazardous wastes.[3−7] However, these media have insufficiencies preventing their extensive applications to industrial fields; $scCO_2$ with a low dielectric constant is a poor solvent for molecules with large molecular weight and hydrophilicity, and scw with a high critical point leads to the corrosion of materials used for chemical reactors. Supercritical alcohols have recently become of interest, since they are more reactive and less corrosive media compared with scw. Several important chemical operations have been reported, e.g., polymer recycling by depolymerization in sc methanol (scMeOH),[8−10] isomerization reactions in sc ethanol (scEtOH),[11] synthesis of functional carbon nanotubes in scEtOH,[12] recovery of uranium oxides from radioactive wastes by using scEtOH,[13] and hydrogenation reactions without catalysis in sc 2-propanol (scPrOH).[14]

Since the unique properties of sc alcohols should be considerably affected by their microscopic behavior, technologies using sc alcohols can be expected to be further developed by understanding the molecular interactions of alcohols under sc conditions. Hence, various spectroscopic and theoretical analyses for the degree of hydrogen bonding have been made on pure alcohols in wide temperature and pressure ranges; these include X-ray,[15] neutron diffraction,[16] IR absorption,[17,18] Raman scattering,[19,20] NMR,[21−25] and dielectric relaxation[26] analyses, and molecular simulations.[27] These studies have clarified that the hydrogen bonds of monohydric alcohols still exist even under sc conditions.

Although much information on static structural properties of sc alcohols is available, static studies cannot be used to illuminate the complicated behavior on various timescales in sc alcohol molecules. The dynamical studies can provide valuable insights into the lifetime of hydrogen bond structures or rate of molecular motions of alcohols. A high temperature and pressure nuclear magnetic resonance (NMR) method which can detect the variation of molecular interactions is suitable for characterizing the complicated behavior of both OH and hydrocarbon (CH_n) groups in self-associated alcohol molecules in liquid and sc states. Actually, NMR spin−echo techniques have been applied to evaluate the reorientational relaxations of OD and CD vectors in deuterated MeOH or EtOH from liquid to sc states.[24,28] We have already developed a multinuclear NMR apparatus, which can measure ^{1}H and ^{17}O NMR relaxations of hydrogen bonded compounds such as water, MeOH, and EtOH in wide temperature and pressure ranges.[24,29] However, it is still unclear at the molecular level about how temperatures, pressures, and fluorinations of alkyl groups affect the dynamic properties invoking translational and rotational motions in alcohols, and to what extent the correlation between intramolecular and intermolecular interactions in sc alcohols is different from that in liquid alcohols.

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In the present study, we have measured the ^1H NMR chemical shifts (δ_H) and ^1H and ^2H NMR spin−lattice relaxation times (^1H- and ^2H-T_1) of MeOH ($T_c = 512.6$ K, $P_c = 8.09$ MPa. $\rho_c = 0.272$ g cm^{-3}), EtOH ($T_c = 513.9$ K, $P_c = 6.14$ MPa. $\rho_c = 0.276$ g cm^{-3}), and PrOH ($T_c = 508.3$ K, $P_c = 4.76$ MPa. $\rho_c = 0.273$ g cm^{-3}), in the temperature range of 298−673 K at reduced pressures ($P_r = P/P_c$) of 1.23 and 3.14 by using high-pressure and high-temperature NMR. Moreover, we have also investigated some fluoroalcohols, in which the electron-withdrawing effect of the fluorine-substituted methyl group makes the oxygen atom of alcohols more acidic compared with nonfluorinated analogues, to elucidate the relation between intramolecular and intermolecular interactions of sc alcohols. The δ_H and ^1H- and ^2H-T_1 values of 2,2,2-trifluoroethanol (TFE, $T_c = 499.3$ K, $P_c = 4.87$ MPa. $\rho_c = 0.484$ g cm^{-3}) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, $T_c = 461.6$ K, $P_c = 3.73$ MPa. $\rho_c = 0.568$ g cm^{-3}), which are known to be important cosolvents in protein folding studies,[30] were examined in the same range as those for EtOH and PrOH. On the basis of the NMR results, we elucidated the effects of temperature, pressure, steric hindrance owing to alkyl chains, and fluorination on intramolecular and intermolecular hydrogen bonding abilities and dynamic properties of these self-associated alcohol molecules.

Experimental Section

Anhydrous MeOH, EtOH, PrOH, TFE, and HFIP (Wako Pure Chemical Ind. Ltd.) were degassed through a number of freeze−pump−thaw cycles. The deuterated alcohols, MeOH-d_4 (CD_3OD, 99.96%), EtOH-d_6 (CD_3CD_2OD, 99.96%), and PrOH-d_8 ($(CD_3)_2CDOD$, 98.0%), TFE-d_3 (CF_3CD_2OD, 99.5%), and HFIP-d_2 ($(CF_3)_2CDOD$, 99.5%), were purchased from ISOTEC Inc. and used without further purification. A high-pressure sapphire cell (Alpha Engineering Ltd.) was filled with each sample under an argon atmosphere, and ^1H and ^2H NMR measurements were carried out with a JEOL JNM-LA300WB spectrometer at 300.4 MHz for the proton frequency and 46.1 MHz for the deuterium frequency, respectively at $P_r = 1.23$ and 3.14 in the temperature range of 298 to 673 K without spinning. The high-temperature and -pressure multinuclear NMR apparatus used in the present study has been already reported previously.[29] The temperature was controlled using a JEOL NM-LVT variable temperature controller, and the sample was heated by nitrogen gas flowing along the outside of the tube. The sample temperature was calibrated with a thermocouple placed just below the sample cell and controlled within ±1.4 at 673 K by using an auxiliary heater. The high-pressure sapphire cell had a 3 mm inner diameter, 10 mm outer diameter, and 154 mm length and made it possible to measure NMR spectra up to around 40 MPa. Pressure to the cell was exerted by an ISCO syringe pump with a precision of ±0.1 MPa at 40 MPa. A sapphire plug was inserted into the sapphire cell to restrict sample convection and to adjust sample volume to approximately 150 μL. It was confirmed that the influence due to corrosion of sapphire is negligible under our experimental conditions, since no aluminum species generated from sapphire was observed for the less than detection limit.[29] All relaxation time measurements were carried out by the inversion recovery method, $\pi-\tau-\pi/2-5T_1$, changing τ values from 10 ms to about 120 s.

Results and Discussion

Proton Chemical Shifts of Alcohols. We measured the ^1H NMR spectra of MeOH, EtOH, and PrOH to investigate the molecular structures and the effects of alkyl groups on self-associating structures in the temperature region from 298 to 673 K at $P_r = 1.23$ and 3.14. It was found that the ^1H NMR signals of the OH proton in MeOH, EtOH, and PrOH shift to higher field with decreasing density until sc conditions, while the chemical shift (δ_H) values of the CH_3 protons were kept almost constant in the range from liquid to sc states. When the δ_H values of the CH_2 protons in EtOH and CH proton in PrOH were recorded relative to the CH_3 protons, the δ_H values settled to a constant value within 0.1 ppm. Namely, the CH_3 proton signals of MeOH, EtOH, and PrOH were found to be used as an internal standard for eliminating effects of differences in the bulk magnetic susceptibility. The δ_H values for alcohols at ambient temperatures and pressures were normalized as 0 ($\delta_{int} = 0$), and the differences ($\Delta\delta_H$) between δ_H values at each density and δ_{int} were plotted as a function of reduced density ($\rho_r = \rho/\rho_c$) as shown in Figure 1. The density was determined by the modified Peng−Robinson equation.[31] We found that the magnitude of the $\Delta\delta_H$ values decreased in order of PrOH > EtOH > MeOH, and the density dependence of H_2O was the largest. The reduction of the $\Delta\delta_H$ values should correspond to loss of hydrogen bonding, because the electron density around the proton atoms in alcohols increases with the hydrogen bond breaking. Therefore, we extrapolated the $\Delta\delta_H$ values to $\rho = 0.01$ g cm^{-3} as shown in Figure 1 and examined the degree (X_{HB}) of hydrogen bonding. The $X_{HB} = 0$ and $X_{HB} = 1$ were determined for the single individual molecule with no hydrogen bonding ($\rho = 0.01$ g cm^{-3}) and for condensed liquid phase molecules at the ambient temperatures and pressures, respectively. We could obtain relational equations between X_{HB} and $\Delta\delta_H$ as follows:

$$X_{HB} = 0.207\Delta\delta_H + 0.663(\text{MeOH}) \quad (1)$$

$$X_{HB} = 0.203\Delta\delta_H + 0.157(\text{EtOH}) \quad (2)$$

$$X_{HB} = 0.189\Delta\delta_H + 0.214(\text{PrOH}) \quad (3)$$

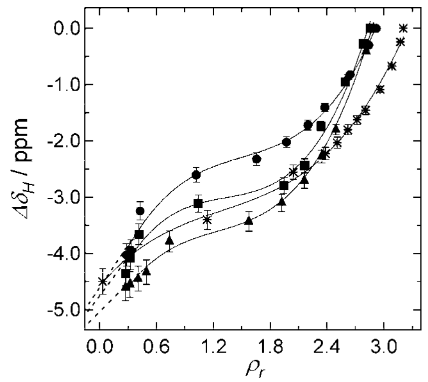


Figure 1. The plots of $\Delta\delta_H$ values vs ρ_r (= ρ/ρ_c) for H_2O (*), MeOH (●), EtOH (■), and PrOH (▲). The $\Delta\delta_H$ values of H_2O quoted are from our previous NMR results.[23] The ρ_r values were determined by the modified Peng−Robinson equation.[31] The dashed lines are extrapolations to $\rho = 0.01$ g cm^{-3} of the solid fitted lines.

The above results were in good agreement with ^1H NMR results of Hoffmann and Conradi.[21] The X_{HB} values were determined as 0.46, 0.37, and 0.29 under the sc conditions of 523 K and $P_r = 1.23$ ($\rho = 0.28$ g cm^{-3}), and the magnitude of X_{HB} values depended on the steric configuration of the functional groups in these alcohols. The X_{HB} values of alcohols were larger than that of H_2O, which was estimated as 0.22 even at $\rho = 0.17$ g cm^{-3}. These results indicated that hydrogen bonding of alcohols as well as water decreased continuously with changes in density from liquid to sc states, and that the X_{HB} values

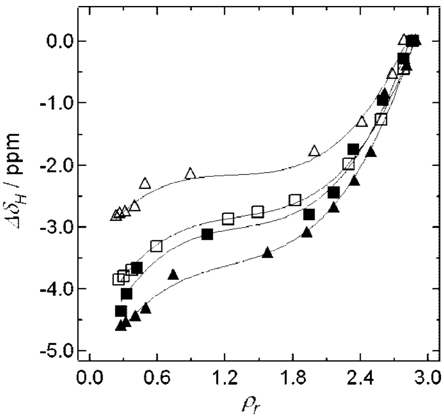
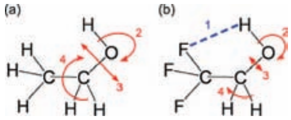


Figure 2. Curves of $\Delta\delta_H$ vs ρ_r for EtOH (□), PrOH (△), TFE (■), and HFIP (▲).

SCHEME 1: Schematic Illustration of Intramolecular and Intermolecular Hydrogen Bonds of (a) EtOH and (b) TFE[a]



[a] 1: intramolecular H−F hydrogen bonding, 2: rotational motion of OH group, which depends strongly on changes in intermolecular hydrogen bonding. 3: C−O bond motion, 4: an internal rotation of CH_2 groups around C−C or C−O bonds.

became lower in the order of MeOH > EtOH > PrOH > H_2O. In general, alcohol molecules with a one-dimensional linear chain structure have a lower energy for breaking hydrogen bonds compared with H_2O which has a three-dimensional shape structure. Furthermore, as the size of the alkyl groups increases in the order of MeOH, EtOH, PrOH, the hydrophobicity of the groups induces the development of self-associated alcohol clusters. Accordingly, the order of MeOH > EtOH > PrOH > H_2O for X_{HB} observed here is due to the intermolecular hydrogen bonding force and hydrophobicity of one of the alkyl groups.

Fluorination Effects on Proton Chemical Shifts. To elucidate the correlation between intramolecular and intermolecular interactions in liquid and sc alcohols, we examined the effects of substituting electronegative CF_3 groups for CH_3 groups. The $\Delta\delta_H$ values of OH groups in TFE and HFIP were measured and found to shift to higher field with decreasing density as shown in Figure 2. Here, the $\Delta\delta_H$ values of OH groups in TFE and HFIP were referenced to CH_2 and CH groups, respectively, because the $\Delta\delta_H$ values of CH_2 and CH groups were constant regardless of changes in densities from liquid to sc states. This result could be interpreted to the cleavage of hydrogen bonding of fluoroalcohols proceeding continuously in a similar manner for nonfluorinated analogues such as EtOH and PrOH. However, the $\Delta\delta_H$ values in fluoroalcohols changed abruptly unlike those in nonfluoroalcohols with the reduction of density. Intermolecular hydrogen bonding is weakened by the formation of intramolecular H−F hydrogen bonding in fluoroalcohols as illustrated in Scheme 1. The strength of intramolecular H−F interactions should be reflected as a variation in the *J*-coupling constant of hydrocarbon groups in ^1H NMR spectra of fluoroalcohols, because the *J*-coupling constant is related to the intermolecular distances.[32] As seen from Figure 3a, the *J* value of CH_2 groups in TFE changes with an increase in temperature at a constant pressure. Figure 3b shows plots of ^3J(H,F) values of TFE and ^3J(H,H) values of EtOH against temperature at a constant pressure. It was found that the ^3J(H,F) values of TFE decrease sharply at the critical temperature, and that the ^3J(H,H) values of EtOH are almost constant for all measurement regions. Thus, the marked decrease in ^3J(H,F) values observed here must be evidence of a decrease in distance between the proton of the OH groups and the fluorine atoms of the CF_3 groups in TFE caused by HF interactions under sc conditions.

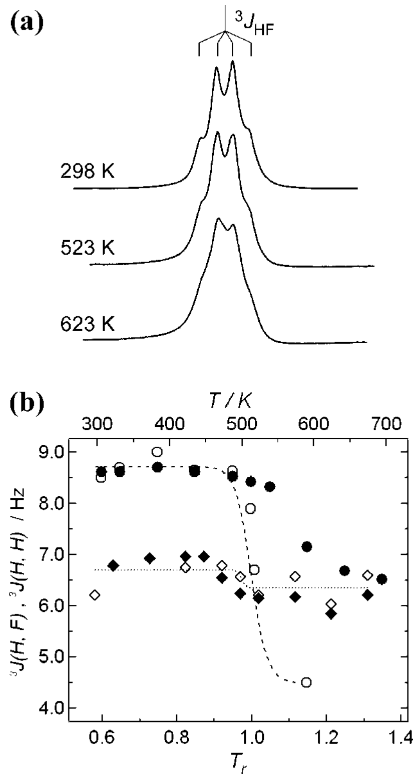


Figure 3. (a) ^1H NMR spectra of CH_2 groups in TFE at 298, 523, and 623 K. (b) Temperature-dependence of ^3J(H,F) and ^3J(H,H) values of CH_2 groups in TFE (●, ○) and in EtOH (◆, ◇), respectively, at a constant pressure. The solid and open symbols refer to $P_r = 3.14$ and $P_r = 1.23$, respectively. The dashed and dotted lines are nonlinear regression fits to the data at $P_r = 1.23$.

Molecular Motions of Alcohols. Measurements of chemical shift cannot be utilized to interpret complicated dynamic properties of each group in alcohols. Therefore, the $1/T_1$ values of ^1H (^1H-$1/T_1$) in MeOH, EtOH, and PrOH were measured by the inversion recovery method in the temperature range of 298 to 673 K at $P_r = 1.23$ to examine molecular motions of each alcohol and steric hindrance effects of alkyl groups. Plots of the ^1H-$1/T_1$ values of these alcohols vs the reduced temperature ($T_r = T/T_c$) are shown in Figures 4a−c. The ^1H-$1/T_1$ values of OH and hydrocarbon (CH_n, $n = 1-3$) groups in MeOH, EtOH, and PrOH are found to decrease with an increase in the range of $T_r = 0.6$ to about $T_r = 1.0$ at constant pressure. Under sc conditions, these ^1H-$1/T_1$ values increase inversely with a further increase in temperature. The experimental ^1H-$1/T_1$ values ($1/T_{1exp}$) might be explained by the sum of dipole−dipole (DD) and spin–rotation (SR) relaxation processes, i.e., $1/T_{1exp} = 1/T_{1DD} + 1/T_{1SR}$, as follows. Below the critical temperature ($<T_r = 1.0$), the DD interactions dominate the relaxation mechanism, because the $1/T_{1DD}$ values are dependent on the molecular reorientation correlation time (τ_c) for OH and CH_n groups as expected by eqs 4 and 5).[33,34] The $1/T_{1DD}$ values are combined with both an intramolecular rotational component ($1/T_{1intra}$) and an intermolecular translational one ($1/T_{1inter}$). In other words, an increase in temperature leads to the reductions of τ_c and the reliable self-diffusion coefficient, *D*.

$$\left(\frac{1}{T_1}\right)_{\mathrm{DD}} = \left(\frac{1}{T_1}\right)_{\mathrm{DD}}^{\mathrm{intra}} + \left(\frac{1}{T_1}\right)_{\mathrm{DD}}^{\mathrm{inter}} = \frac{3}{2}\gamma^4\hbar^2\frac{1}{r^6}\tau_{\mathrm{c}} + \frac{\pi N\gamma^4\hbar^2}{5\ aD} \quad (4)$$

$$\left(\frac{1}{T_1}\right)_{\mathrm{DD}}^{-\mathrm{CH}n} = \left(\frac{1}{T_1}\right)_{\mathrm{DD}}^{\mathrm{intra}} + \left(\frac{1}{T_1}\right)_{\mathrm{DD}}^{\mathrm{inter}} = \frac{3}{4}\gamma^4\hbar^2\frac{1}{r^6}\tau_{\mathrm{c}} + 14\gamma^4\hbar^2\frac{1}{d^6}\tau_{\mathrm{c}} \quad (5)$$

Here h is Planck's constant, r is the internuclear distance, γ is the proton gyromagnetic ratio, a is the hydrodynamic radius, d is the distance between the centers of the equilateral triangles formed by the hydrogen atoms in the hydrocarbon groups, N is the number of spins per unit volume, and τ_c is expressed by $4\pi a^3\eta/3kT$ (η: viscosity).

On the other hand, in the sc regions ($T_r > 1.0$), the relaxation processes should be attributed to the SR mechanism. The SR relaxation processes arise from the interaction between the nuclear magnetic moment and the fluctuating magnetic fields generated by the molecular magnetic moment associated with the charge distribution within the molecule. Thus, this interaction contributes to the change in the molecular angular momentum based on molecular collisions. Since the molecular collisional frequency is very low in the high temperature region, the molecular angular momentum exchange correlation time (τ_J) related as $\tau_c\tau_J = I/6kT$ increases. Hence, the ^{1}H-1/T_1 values vary inversely with the temperature as seen from the following equation:

$$\left(\frac{1}{T_1}\right)_{\mathrm{SR}} = \frac{8\pi^2 IkT}{\hbar^2}C_{\mathrm{eff}}^2\tau_J \quad (6)$$

where k is the Boltzmann constant, I is the moment of inertia, and C_{eff} is the effective spin-rotation coupling constant tensor. In the present study, the I values for the principal axes of EtOH and PrOH, which are parallel to the axis of internal rotation, are 5.74×10^{-39} g/cm^3 and 9.89×10^{-39} g/cm^3, respectively.[35,36] On the other hand, in MeOH, 3.53×10^{-39} g/cm^3 was used as the perpendicular component of I, because I value for the principal axis is too small.[37] Unfortunately, calculation of the spin-rotation relaxation time using eq 6 is not usually possible, because the C_{eff} value is not known for many molecules. Herein, we utilized C_{eff} value of CH_4 in place of the values of the pure alcohols.[25,38,39]

The calculated relaxation rates (1/$T_{1\mathrm{cal}}$) were estimated according to eqs 4−6 and compared with the experimental data (1/$T_{1\mathrm{exp}}$). As shown in Figure 4, the temperature-dependence of 1/$T_{1\mathrm{cal}}$ values of OH and CH_3 groups in MeOH was similar to that of 1/$T_{1\mathrm{exp}}$ values from liquid to sc conditions. However, in the case of EtOH and PrOH, the temperature dependence of 1/$T_{1\mathrm{cal}}$ differed from that of 1/$T_{1\mathrm{exp}}$. The 1/$T_{1\mathrm{cal}}$ values of OH groups were in agreement with the 1/$T_{1\mathrm{exp}}$ values, whereas the 1/$T_{1\mathrm{theo}}$ values of CH_n groups were quite different from 1/$T_{1\mathrm{exp}}$ values in the sc conditions ($T_r > 1.0$). It is noteworthy that the 1/$T_{1\mathrm{exp}}$ values of CH_n groups show less temperature dependence in sc conditions compared with the 1/$T_{1\mathrm{cal}}$ values. This discrepancy is resulted from not only the indefinite C_{eff} value of pure alcohols but also the cross-correlation effects between DD interactions of carbon with adjacent protons in CH_n groups.[38] As seen from Scheme 1a, the OH groups depend strongly on the changes of intermolecular hydrogen bonding. On the other hand, since the CH_n groups are essentially dominated by an internal rotation about the C−C and C−O bonds, the internal rotational motions of CH_n groups are enhanced with breaking hydrogen bond under sc conditions (see no. 4 in Scheme 1a). In this case, the cross-correlation effects connected with intramolecular DD interactions of a carbon atom with a proton can play an important role in relaxation processes in CH_n groups. As a result, the temperature dependence of ^{1}H-1/T_1 values of CH_n groups in sc regions becomes obscure unlike those in OH groups.

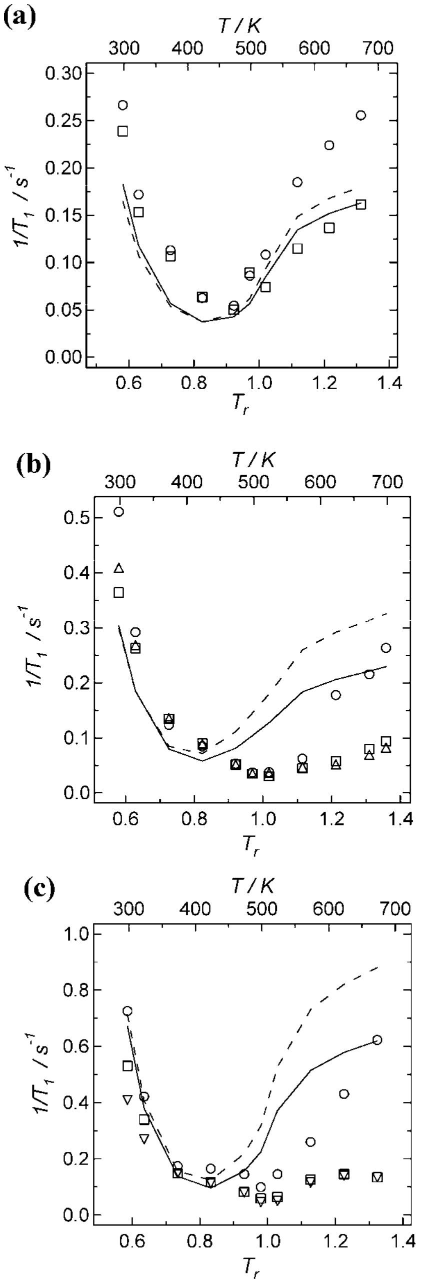


Figure 4. Temperature dependence of experimental and calculated 1/T_1 values of hydroxyl and hydrocarbon groups in (a) MeOH, (b) EtOH, and (c) PrOH at $P_r = 1.23$. The symbols of ○, □, △, and ▽ correspond to OH, CH_3, CH_2, and CH groups, respectively. The solid and dashed lines are values for OH and CH_3 groups calculated from eqs 4−6.

Fluorination Effects on Proton Relaxation Times. If changes in the internal rotation of CH_n groups are caused by intramolecular interactions, the intramolecular DD interactions between proton and fluorine atoms in fluoroalcohols should strongly affect the ^{1}H-T_1 values compared with nonfluoroalcohols under sc conditions. Therefore, we measured the ^{1}H-T_1 values of OH and CH_2 groups in TFE and OH and CH groups in HFIP in the same way as performed for EtOH and PrOH and compared them. The ^{1}H-T_1 values of OH and CH_2 groups in EtOH and TFE and of OH and CH groups in PrOH and HFIP are plotted as a function of T_r at a constant pressure in Figures 5a,b. The relaxation mechanisms for the OH group up to and

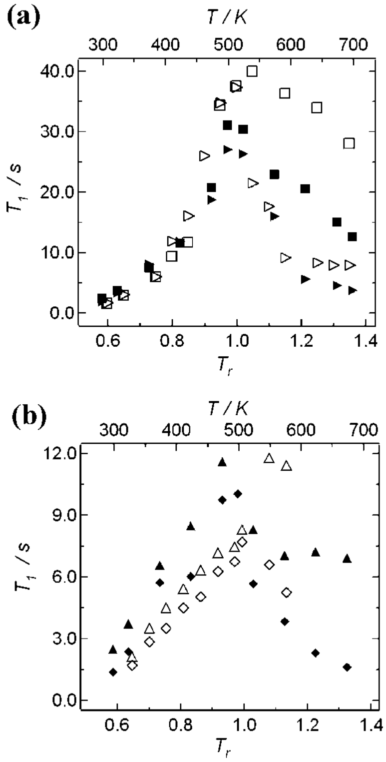


Figure 5. (a) T_1 values for OH (right solid triangle) and CH_2 (■) groups in EtOH and for OH (left open triangle) and CH_2 (□) groups in TFE at $P_r = 1.23$ against temperature. (b) T_1 values for OH (◆) and CH (▲) groups in PrOH and for OH (◇) and CH (△) groups in HFIP at $P_r = 1.23$ against temperature. For HFIP, the data above $T_r = 1.2$ are not shown because of splitting of NMR peaks.

above the critical temperature for fluoroalcohols such as TFE and HFIP could be simply explained by the DD and SR interactions, respectively. This tendency was quite consistent with nonfluorinated systems as mentioned before. However, there is an apparent discrepancy in the ^{1}H-T_1 values of hydrocarbon groups between fluoroalcohols and nonfluoroalcohols under sc conditions, i.e., the ^{1}H-T_1 values of the CH_2 group in TFE and the CH one in HFIP were larger than those in nonfluoroalcohols for sc conditions. This interesting phenomenon should be attributed to changes of rotation of hydrocarbon groups in fluoroalcohols accompanying the H−F DD interactions, because the DD interactions result in an increase of the ^{1}H-T_1 values. For TFE and HFIP, it is considered that their molecular conformation is stabilized by the formation of H−F interactions under sc conditions, and that essentially the rotations of CH_2 and CH groups around the C−O bond are limited as illustrated in Scheme 1. Consequently, it was confirmed that the intramolecular H−F interactions controlled the rotations of fluoroalcohols in sc conditions, indicating lower temperature dependence than for nonfluorinated analogues. This fact supported our interpretation that the ^{1}H relaxation processes for CH_n groups in pure alcohols under sc conditions were affected by cross-correlation effects.

Deuterium Relaxation Times of Deuterated Hydroxyl Groups. It is difficult to evaluate the ^{1}H-T_1 values involving both intramolecular components associated with rotational and translational diffusions. The relaxation processes of ^{2}H nuclei in solutions are mainly dominated by quadrupole interactions; that is, the contribution of the chemical shift anisotropy, scalar coupling, and SR interaction to ^{2}H-T_1 is a few percent.[25] For examining the molecular reorientational relaxation of each group in sc alcohols, it should be meaningful to measure ^{2}H-T_1 of deuterated alcohol with a quadrupole moment. We measured the ^{2}H-T_1 values of deuterated hydrocarbon (CD_n, $n = 1-3$) groups in CD_3OD, CD_3CD_2OD, $(CD_3)_2CDOD$, CF_3CD_2OD, and $(CF_3)_2CDOD$ in the temperature range of 298 to 673 K at $P_r = 1.23$ and 3.14 by using the inversion recovery method. As seen from Figure 6, the ^{2}H-T_1 values of OD groups in these five solutions increase continuously with increasing temperature over the range from liquid to sc states. This means that the relaxation processes of OD groups may be controlled by a quadrupolar mechanism over the range from liquid to sc states. The resulting ^{2}H-T_1 values are related to the reorientational time (τ_c^D) for the motion of the deuterium electric field gradient (EFG) tensor through eq 7:[33,34]

$$\left(\frac{1}{T_1}\right)_Q = \frac{3\pi^2}{2}\left(\frac{e^2Qq}{h}\right)^2 \tau_c^D \tag{7}$$

where e^2Qq/h is the quadrupole coupling constant (QCC) connected with the EFG tensor of a molecule. The value of QCC, which indicates the strength of the interaction between the quadrupole moment of the nucleus (eQ) and the electric field gradient at the nucleus (eq), is given as a measure of the molecular symmetry. The QCC values at ambient conditions for ^{2}H nucleus has been reported as 211 kHz, 181 kHz, and 196 kHz for O−D vectors in CD_3OD, CD_3CD_2OD, and $(CD_3)_2CDOD$, respectively.[39−41] In order to clarify the effects of steric hindrance of alkyl chains and fluorination for reorientational motions in these monohydric alcohols, we estimated the τ_c^D values of OD in CD_3OD, CD_3CD_2OD, $(CD_3)_2CDOD$, CF_3CD_2OD, and $(CF_3)_2CDOD$ by using the known QCC values. Here, the QCC values of CF_3CD_2OD and $(CF_3)_2CDOD$ were replaced by those of CD_3CD_2OD and $(CD_3)_2CDOD$. The temperature dependence of τ_c^D is shown in Figure 7. The τ_c^D values of OD groups for nonfluoroalcohols decreased with an increase in temperature. The τ_c^D values of OD groups were 0.17−5.91 ps in CD_3OD, 0.30−22.4 ps in CD_3CD_2OD, 0.27−26.0 ps in $(CD_3)_2CDOD$, 0.54−33.8 ps in CF_3CD_2OD, and 0.51−29.3 ps in $(CF_3)_2CDOD$ in the temperature range from 298 to 673 K at $P_r = 3.14$. The values at 673 K in CD_3OD, CD_3CD_2OD, and $(CD_3)_2CDOD$ are quite close to the values of the free-rotor correlation time (τ_{free}) expressed by eq 8:[25]

$$\tau_{free} = \frac{2\pi}{9}\left(\frac{I}{kT}\right)^{1/2} \tag{8}$$

where I is the moment of inertia. The τ_{free} values were taken to be 0.14, 0.17, and 0.23 ps in CD_3OD, CD_3CD_2OD, and $(CD_3)_2CDOD$, respectively. This indicated that the rotational motions of alcohols under sc conditions were comparable to those of monometric molecules. Unfortunately, the absolute τ_c^D values evaluated by using the known QCC values have relatively low accuracy in the sc conditions, because the QCC itself can be strongly affected by changes of temperature and pressure. When the protons in CH_3 groups of alcohols were replaced by fluorine, i.e., CF_3CD_2OD and $(CF_3)_2CDOD$ systems, the inflection point appeared at around the critical point. We considered that the appearance of intramolecular H−F interactions resulted in the inhibition of reorientational motions of OD groups for the fluoroalcohols in sc conditions but not for nonfluoroalcohols.

Deuterium Relaxation Times of Deuterated Hydrocarbon Groups. We have to pay attention to the temperature dependence of ^{2}H-T_1 values for deuterated hydrocarbon (CD_n) groups in the alcohols which are not being consistent with the OD systems as shown in Figure 6. Although the ^{2}H-T_1 values increase continuously below the critical temperature, the ^{2}H-T_1 values in CD_n groups are found to approach an almost constant

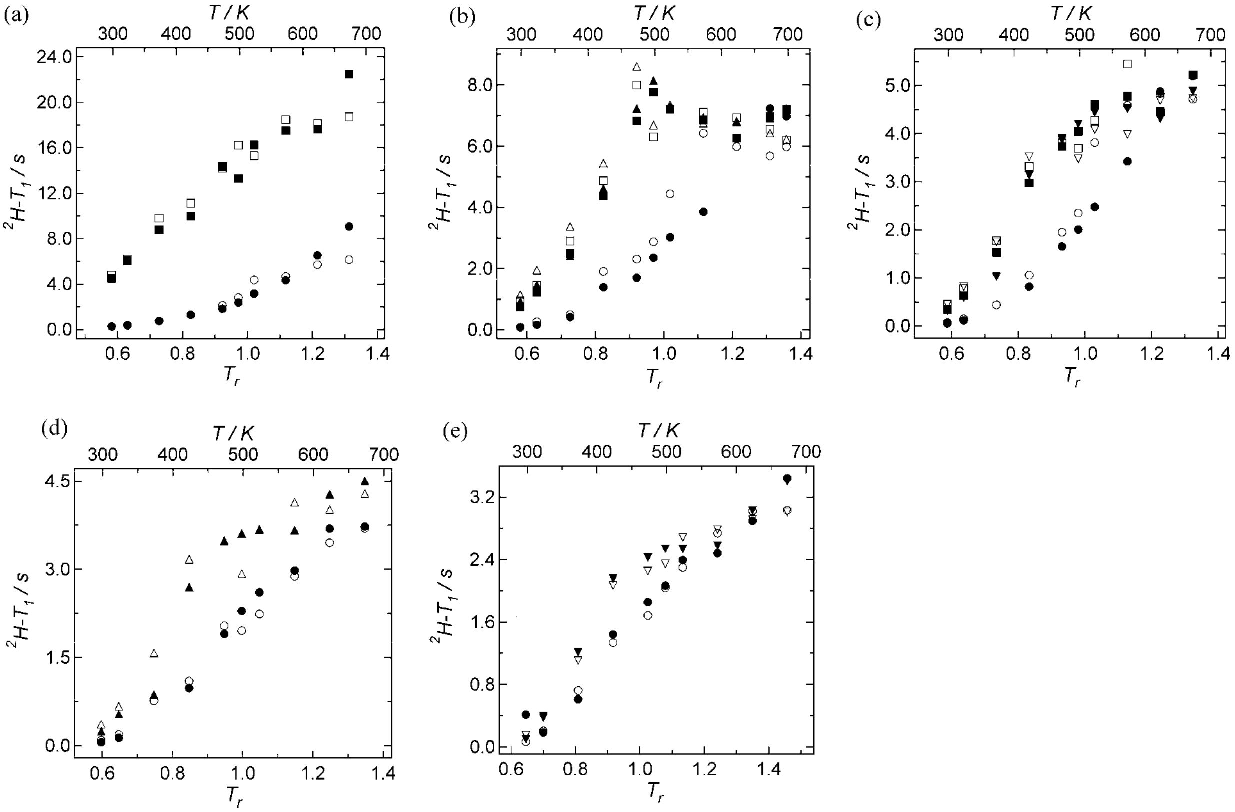


Figure 6. Deuterium T_1 values of (a) CD_3OD, (b) CD_3CD_2OD, (c) $(CD_3)_2CDOD$, (d) CF_3CD_2OD, and (e) $(CF_3)_2CDOD$ as functions of temperature a constant pressure. The shaped and open circles (●, ○), squares (■, □), triangles (▲, △), and inverse triangles (▼, ▽) represent data of OD, CD_3, CD_2, and CD groups at P_r = 3.14 and 1.23, respectively.

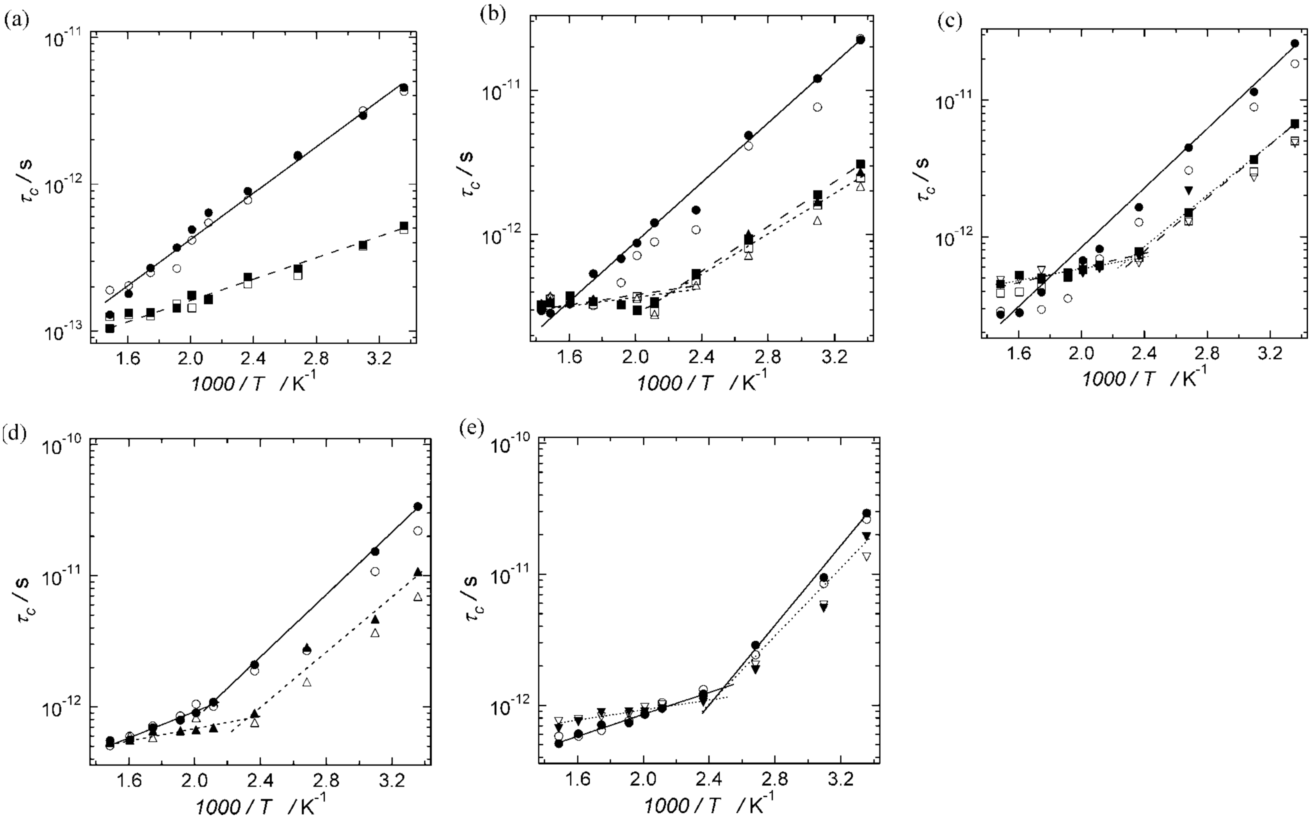


Figure 7. Semilogarithmic plot of τ_c vs the reciprocal temperature for the rotational molecular motion of alcohols. The shaped and open marks correspond to P_r = 3.14 and 1.23, respectively. (a) Hydroxyl (●, ○); methyl (■, □) groups in CD_3OD, (b) hydroxyl (●, ○); methylene (▲, △), methyl (■, □) groups in CD_3CD_2OD, (c) hydroxyl (●, ○); methine (▼, ▽), methyl (■, □) groups in $(CD_3)_2CDOD$, (d) hydroxyl (●, ○); methylene (▲, △) groups in CF_3CD_2OD, and (e) hydroxyl (●, ○); methine (▼, ▽) groups in $(CF_3)_2CDOD$. The solid, dashed, and dotted lines are least-squares fit to the data.

TABLE 1: Apparent Activation Energies (ΔE_a, kJ mol^{-1}) of Internal Rotations of Deuterated Hydroxyl (OD) and Hydroxycarbon Groups (CD_n) in CD_3OD, CD_3CD_2OD, $(CD_3)_2CDOD$, CF_3CD_2OD, and $(CF_3)_2CDOD$

		$P_r = 3.14$		$P_r = 1.23$	
groups	solvent	$<T_c$	$>T_c$	$<T_c$	$>T_c$
OD	CD_3OD	15.2		13.6	
	CD_3CD_2OD	19.8		18.5	
	$(CD_3)_2CDOD$	20.8		20.6	
	CF_3CD_2OD	22.8	9.6	20.2	9.4
	$(CF_3)_2CDOD$	29.1	7.9	28.9	8.8
CD_n	CD_3OD (CD_3)	7.0		6.8	
	CD_3CD_2OD (CD_2)	13.6	2.9	13.3	0.9
	CD_3CD_2OD (CD_3)	14.8	3.3	13.9	2.3
	$(CD_3)_2CDOD$ (CD)	17.9	4.0	17.0	2.7
	$(CD_3)_2CDOD$ (CD_3)	18.5	5.2	16.5	6.1
	CF_3CD_2OD (CD_2)	20.4	4.6	19.1	3.3
	$(CF_3)_2CDOD$ (CD)	24.9	3.8	24.8	3.7

value above the critical temperature ($T_r = 1.0$) with the exception of CD_3OD. Here, we roughly estimated the τ_c^D values of CD, CD_2, and CD_3 groups according to eq 7, in which the QCC value of 170 kHz for C−D vectors in the monohydric alcohols was used;[42] this allowed us to discuss the differences in reorientational motions between O−D and C−D bonds. As shown in Figure 7, in the range from ambient temperatures to around T_c, the τ_c^D values decreased by a factor of about 1/5 to 1/10 in the temperature range from 25 to 400 °C at $P_r = 3.14$, i.e., from 0.52 to 0.11 ps for the CD_3 group in CD_3OD, from 2.66 to 0.33 ps and from 3.08 to 0.33 ps for CD_2 and CD_3 in CD_3CD_2OD, from 6.68 to 0.46 ps and from 6.72 to 0.45 ps for CD and CD_3 in $(CD_3)_2CDOD$, from 10.5 to 0.52 ps for CD_2 in CF_3CD_2OD, and from 19.8 to 0.68 ps for CD in $(CF_3)_2CDOD$, respectively. Above T_c, the τ_c^D values of CD_n groups in alcohols studied here were almost constant. Such phenomena suggested that the internal rotations of the CD_n groups were not modulated by the reduction of the degree of hydrogen bonding of alcohols under sc conditions. These results indicated that the relaxation processes for the CD_n groups under sc conditions are not determined by quadrupole interactions but by the cross-correlation effects in DD interactions of C−D bonds. Assuming that the rotational relaxation process of alcohols is thermally activated, and then the apparent activation energy (ΔE_a) can be obtained from the following Arrhenius-type relation:

$$\tau_c^D = \tau_0 \exp(\Delta E_a/RT) \tag{9}$$

where R is the gas constant (8.3145 J K^{-1} mol^{-1}). The ΔE_a values for OD groups in CD_3OD, CD_3CD_2OD, $(CD_3)_2CDOD$, CF_3CD_2OD, and $(CF_3)_2CDOD$ were calculated from the plots of $ln\tau_c^D$ vs the reciprocal temperature (See Figure 7), and are listed in Table 1. The ΔE_a values for the OD groups increased in the order of CD_3OD, CD_3CD_2OD, and $(CD_3)_2CDOD$. However, the order was quite opposite that seen for X_{HB} values. These phenomena indicated that the cleavage of hydrogen bonding for monohydric alcohol molecules was not caused by rotational motion of hydroxyl groups but mainly depends on the fluctuational motion of the alcohol itself. Actually, in the case of CF_3CD_2OD and $(CF_3)_2CDOD$, an inflection point appeared in the plots of $ln\tau_c^D$ vs the reciprocal temperature. The ΔE_a values below and above the critical point were more than 20 kJ mol^{-1} and less than 10 kJ mol^{-1}, respectively. Such changes in ΔE_a values for fluorination systems could be due to the enhancement of hydrogen bond breaking accompanied by H−F intramolecular interactions.

On the other hand, the plots of $ln\tau_c^D$ vs the reciprocal temperature for all CD_n groups in CD_3OD, CD_3CD_2OD, $(CD_3)_2CDOD$, CF_3CD_2OD, and $(CF_3)_2CDOD$ were represented by two straight lines as shown in Figure 7. We found a distinct difference in the ΔE_a values above and below the critical temperatures, and the ΔE_a values for CD_n groups in every compound were much lower than those for OD groups as seen from Table 1. The ΔE_a values in sc conditions were several times lower than those in liquid conditions, indicating that the internal rotational barrier of CD_n groups is lowered by enhancement of the degrees of freedom for the molecular rotation with a decrease in density. The magnitude of ΔE_a values, which increased in the order of CD_3OD, CD_3CD_2OD, and $(CD_3)_2CDOD$, was consistent with that of surface area of hydrophobic alkyl groups.[43] This solvent dependence meant that the intermolecular interactions between hydrophobic alkyl groups and/or steric hindrance enhanced the potential energy barrier for internal rotation.

Conclusions

We examined the ^{1}H-δ_H, ^{1}H-T_1, and ^{2}H-T_1 values of MeOH, EtOH, PrOH, TFE, and HFIP from liquid to sc states to determine the effects of temperature, pressure, and fluorine substitution on the structural and dynamic properties of the alcohol molecules by using high-pressure and high-temperature NMR spectroscopy. We found that the degree of hydrogen bonding (X_{HB}) of the alcohols decreased continuously with an increase in temperature, and that hydrogen bonding still remained even in sc conditions. The magnitude of X_{HB} values was found to decrease in the order of MeOH > EtOH > PrOH and was larger than that of H_2O in sc conditions. The hydrogen bonding of sc alcohols was significantly influenced by the intramolecular H−F interactions accompanied by fluorination of CH_3 groups, which were proved by the differences in J-coupling constant (^3J) between EtOH and TFE. In addition, on the basis of the results that the temperature dependence of ^{1}H-T_1 values was reversed below and above T_c, we elucidated that the relaxation processes of OH groups in MeOH, EtOH, and PrOH could be expressed by DD and SR mechanisms in liquid and sc states, respectively. In the case of CH_n groups, the temperature dependence of ^{1}H-T_1 values below T_c was similar to that of OH systems, while the ^{1}H-T_1 values approached almost constant values in sc conditions. These phenomena suggested that the cross-correlation effects connected with intramolecular DD interactions between a carbon atom and an adjacent proton of CH_n groups in monohydric alcohols were associated with the T_1 relaxation mechanism under sc conditions. This interpretation was supported by the results that the intramolecular H−F DD interactions for TFE and HFIP led to the inhibition of the internal rotation of CH and CH_2 groups unlike for nonfluoroalcohols. Moreover, to determine the intramolecular rotational motions, the measurements of ^{2}H-T_1 values for these alcohols were also carried out in liquid and sc states. The results showed that the linear temperature dependence of ^{2}H-T_1 values for OD groups were quite different from the temperature dependence for CD_n systems with the inflection points at around T_c and that above T_c, the CD_n groups had almost constant ^{2}H-T_1 values. Such results indicated that the internal rotations of the CD_n in sc conditions were too fast to modulate intra- and intermolecular interactions of alcohols. Namely, the dominant relaxation mechanism for sc alcohols could be interpreted to be cross-correlation effects rather than quadrupolar relaxation. By utilizing the ^{2}H-T_1 values, we roughly estimated the molecular reorientational correlation times (τ_c^D) of OD and

CD_n groups. The τ_c^D values of OD groups in CD_3OD, CD_3CD_2OD, and $(CD_3)_2CDOD$ decreased continuously with increasing temperature and were close to the correlation time corresponding to a free-rotor in sc regions. The fluorination of such alcohols, i.e., CF_3CD_2OD and $(CF_3)_2CDOD$, enabled the temperature dependence of τ_c^D values to be lowered in sc regions, because of the appearance of intramolecular H−F interactions. Comparing the temperature dependence of τ_c^D for CD_n groups with that for OD groups, the distinct difference was seen in sc conditions that the CD_n groups in CD_3CD_2OD, $(CD_3)_2CDOD$, CF_3CD_2OD, and $(CF_3)_2CDOD$ approached an almost constant τ_c^D value above T_c with the exception of CD_3OD. The ΔE_a values for the molecular reorientational motions in these alcohols were calculated and found to decrease about 1 order of magnitude compared with those for liquid alcohols. Accordingly, we concluded that molecular motions for OH groups of monohydric alcohols were controlled by intermolecular hydrogen bonding structures from liquid to sc regions, while in CH_n groups of alcohols the interactions for controlling the molecular motions shifted from intermolecular interactions in liquids states to intramolecular interactions such as cross-correlation effects between a carbon atom and an adjacent proton and H−F hydrogen bonding in sc states.

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