

^1H Spin-Lattice Relaxation Times of Water, Methanol, and Ethanol under Sub- and Supercritical Conditions

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^1H NMR spin-lattice relaxation times (T_1) of water, methanol, and ethanol (abbreviated as W.M.E) were measured in the range of 25 to 400 °C at 30, 20, and 20 MPa, respectively by using high-pressure NMR. It was found that the T_1 values for each group of W.M.E increase with an increase in temperature up to around 220, 160, and 170 °C, and that above these temperatures, the T_1 values decrease and approach a constant value at 300, 200, and 220 °C, respectively. It is explained that the spin-lattice relaxation (SLR) processes are dominated by the dipole-dipole (DD) mechanism at lower temperature and by the spin-rotation (SR) mechanism at higher temperatures. The reasons that the T_1 values are nearly constant are supposed.

In recent years, supercritical fluids (SCF) have become of interest as alternative solvents for chemical reactions and separations.^{1,2} Thus, the properties of SCF, especially, the intermolecular interactions in SCF have been investigated extensively.³⁻⁵ For such studies, high-pressure NMR has been used as one of powerful tools.^{6,7} Recently, the hydrogen-bonding interactions in supercritical W.M.E were examined by NMR.⁸⁻¹² It was shown that the extent of hydrogen-bonding in W.M.E at near-critical conditions is 30% of that at room temperature. However, limited information is available concerning the molecular interactions in W.M.E under supercritical conditions.^{11,13} Hence, we measured the T_1 values of W.M.E under sub- and supercritical conditions.

High-pressure ^1H NMR was measured with a JEOL JNM-LA300WB spectrometer at 300.4 MHz. The high-pressure NMR equipment was designed according to the previous paper.¹⁴ A sapphire glass tube with 1.5 mm inner diameter, 5 mm outer diameter, and 150 mm long (Alpha Engineering Ltd.) was used as a high-pressure NMR cell. The probe temperature was controlled by JEOL NM-LVT variable temperature controller. Pressure to the NMR cell was exerted with ISCO syringe pump (Model-260D). Anhydrous methanol and ethanol (Wako Pure Chem. Ind. Ltd.) were used without further purification. The deuterium (D) isotope effects were examined by using D_2O , CD_3OD , and $\text{CD}_3\text{CD}_2\text{OD}$ (ISOTEC Inc., 99.96 %). All samples were degassed by bubbling Ar gas.

The T_1 values of water (OH group), methanol (CH_3 and OH groups), and ethanol (CH_3 , CH_2 , and OH groups) were measured by the inversion recovery method in the range of 25 to 400 °C at 30, 20, and 20 MPa, respectively. The results are shown in Figures 1, 2, and 3. In these figures, the reduced temperature are also shown. The T_1 values for each group of W.M.E increase with an increase in temperature up to around 220, 160, and 170 °C, respectively. Above these temperatures, the T_1 values decrease and approach a constant value at 300, 200, and 220 °C, respectively.

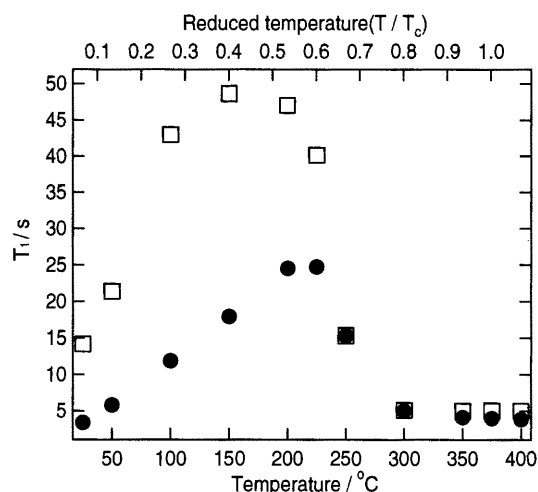


Figure 1. Proton spin-lattice relaxation times (T_1) of water (●:normal, □:including 95% D_2O) as a function of temperature.

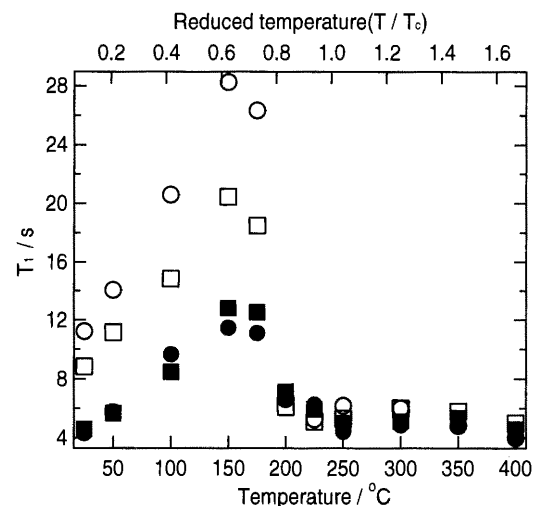


Figure 2. Proton spin-lattice relaxation times (T_1) of OH (●:normal, ○:including 95% CD_3OD) and CH_3 (■, □) groups of methanol as a function of temperature.

In the region where the T_1 values increase with an increase in temperature (<220 °C in Figure 1, <160 °C in Figure 2, and <170 °C in Figure 3), the SLR processes may be explained by the DD mechanism, because in this mechanism the SLR process is dependent on the molecular reorientation correlation time (τ_c), which decreases with increasing temperature. On the

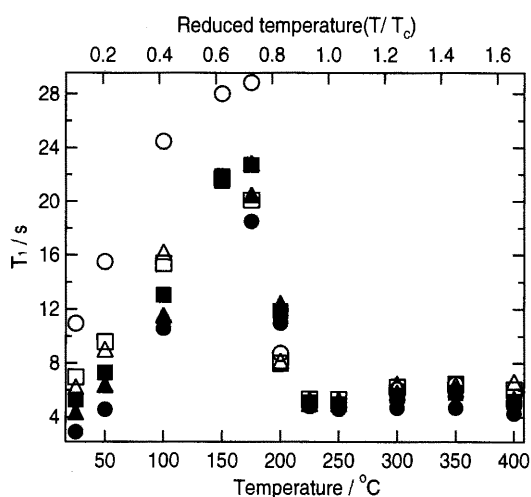


Figure 3. Proton spin-lattice relaxation times (T_1) of OH (●: normal, ○: including 95% $\text{CD}_3\text{CD}_2\text{OD}$), CH_2 (▲, △), and CH_3 (■, □) groups of ethanol as a function of temperature.

other hand, in the range where the T_1 values decrease with increasing temperature (220 - 300 °C in Figure 1, 160 - 200 °C in Figure 2, and 170 - 220 °C in Figure 3), the SLR processes may be attributed to the SR mechanism as follows. The SR relaxation arises 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 correlates with the change in the molecular angular momentum due to molecular collisions. The densities of W.M.E decrease with increasing temperature at a constant pressure and the molecular collisional frequency decreases. This leads to the increase in the molecular angular momentum exchange correlation time (τ_c) and hence the T_1 values become small as the temperature increases.

In order to confirm validity of the above interpretation that the SLR processes are dominated by the DD mechanism at lower temperatures and by the SR mechanism at higher temperatures, the D isotope effects on T_1 values of W.M.E were examined using samples of (5% H_2O + 95% D_2O in volume), (5% CH_3OH + 95% CD_3OD), and (5% $\text{CH}_3\text{CH}_2\text{OH}$ + 95% $\text{CD}_3\text{CD}_2\text{OD}$). The changes in electron densities by the D substitutions are not so large and hence the D isotope effect in the SR interactions should be relatively small. However, the deuterations should increase the T_1 values when the DD interaction is dominant, because the nuclear magnetic moment of D is one-third of the nuclear magnetic moment of H. On the basis of these considerations, it is expected that the T_1 values in the deuterated systems become longer than those in the non-deuterated ones at lower temperature region and they do not change at

higher temperatures. The results are shown in Figures 1, 2, and 3, and consistent with the above expectation.

It should be noticed that near or above the critical temperatures the T_1 values little change with temperature and the D isotope effects are not observed, and that these phenomena are extremely similar in W.M.E. Furthermore, the T_1 values in water were found to be almost constant (4.5 ± 0.5 s) without depending on pressure in the range of 22 to 35 MPa at 400 °C. This means that the SLR process in water in this region is independent of the density, because the density should increase with increasing pressure at a constant temperature. This is obviously different from the results of Jonas¹³ that the T_1 values increase linearly with an increase in density above the critical temperature and within the density range less than 0.75 g cm^{-3} .

The present results that the T_1 values are independent of temperature under the supercritical conditions rule out the intermolecular interactions for the ^1H SLR processes of W.M.E under supercritical conditions. It is interesting that the temperature where the T_1 values become nearly constant at around 5 s for water, methanol, and ethanol is about 0.8 reduced temperature. More detail analyses are in progress.

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