A Unique Concentration Dependence of NMR Longitudinal Relaxation Time of Water in Supercritical Carbon Dioxide

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^{1}H NMR longitudinal relaxation times (T_1^{obs}) of water in supercritical carbon dioxide were precisely measured as a function of water concentration (c) at 313.3 K and at 10 and 20 MPa. $1/T_1^{obs}$ linearly decreased with increasing c up to ~12 mol m^{-3}, and then was less sensitive to c. Because the spin-rotation interaction is the predominant mechanism in T_1^{obs}, the concentration dependence reflects a change in the hydrogen bonding structure between water molecules in the solutions.

Water and carbon dioxide are the most fundamental and essential elements for our lives. Although there have been a number of reports on aqueous solutions of CO_2 (carbonated water), only a few studies[1] have been carried out for the system of CO_2-rich phase with a small content of H_2O. Moreover, environmentally-acceptable supercritical carbon dioxide (sc-CO_2) has recently been used as reaction media as well as extraction media.[2] A small amount of H_2O dissolved in sc-CO_2 played an important role in biochemical[3] and organometallic[4] reactions, but the mechanism has still remained unrevealed. In order to investigate the mechanism of hydrogen bonding formation between H_2O molecules in CO_2-rich solutions as well as the dynamic effects of H_2O on such specific reactions, we have determined ^{1}H NMR relaxation times of H_2O as a function of concentration in sc-CO_2.

High-resolution ^{1}H NMR spectra were recorded with a standard Varian Inova 500 spectrometer at 499.9 MHz by using the temperature-controllable high-pressure cell, which has recently been established for the precise measurements of supercritical solutions.[5] Over the experiments, the sample temperature in the high-pressure cell was kept 313.3 K within ± 0.2 K. Paramagnetic oxygen dissolved in water was degassed by passing carefully through 5 MPa of solvent gas (99.9% up, Sumitomo Seika Chemicals Co.) into the solute liquid. The sample solution was prepared in the mixing vessel outside the magnet, and then was introduced into the high-pressure cell. The concentration was quantitatively determined from the relative peak area of the solute protons to that of the TMS protons that were sealed into the capillary tube in the high-pressure cell. The relaxation times (T_1) were measured by the conventional inversion recovery method with a pulse delay being longer than $5T_1$. The experimental procedure was described in detail elsewhere.[5]

The reciprocals of the observed relaxation times (T_1^{obs}) of H_2O in sc-CO_2 at 313.3 K and at 10 and 20 MPa were plotted against the concentration (c) of H_2O in Figure 1 (open symbols). The concentration dependence and the pressure dependence were statistically significant beyond the experimental errors. As shown in Figure 1, $1/T_1^{obs}$ linearly decreased with increasing c up to ~12 mol m^{-3} and remained almost unchanged at higher c. The linear portion was expressed by

$$1/T_1^{obs} = 1/T_1^{\infty}\,(1 + Bc)\,. \qquad (1)$$

Here, T_1^{∞} corresponds to the relaxation time at infinite dilution (0.257 ± 0.012 and 0.160 ± 0.004 s^{-1} at 10 and 20 MPa, respectively) and B is a linear coefficient (-0.051 ± 0.011 and -0.036 ± 0.005 mol^{-1} m^3 at 10 and 20 MPa, respectively), where the uncertainties are given by the 95% confidence limit.

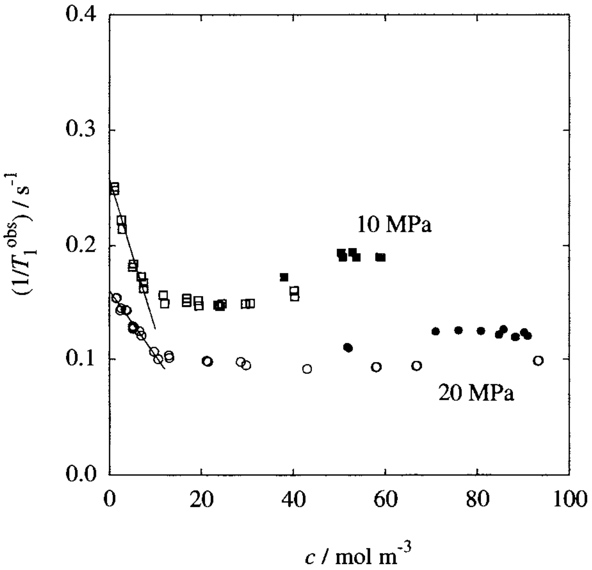

Figure 1. Concentration dependence of ^{1}H relaxation times of water in sc-CO_2 at 313.3 K and at 10 and 20 MPa. Open and closed symbols represent normal and D_2O-diluted (0.05 H_2O + 0.95 D_2O) water, respectively.

The observed relaxation time should be mainly dominated by the spin-rotation interaction and the intramolecular and intermolecular magnetic dipole–dipole interactions. When we consider the dipole–dipole interactions, the rotational correlation time (τ_r) and the translational diffusion coefficient (D_t) of H_2O in sc-CO_2 play an important role in the intramolecular relaxation time ($T_{1,\,dd}$(intra)) and the intermolecular relaxation time ($T_{1,\,dd}$(inter)), respectively;[6] that is, $1/T_{1,\,dd}(\text{intra}) \propto \tau_r$ and $1/T_{1,\,dd}(\text{inter}) \propto 1/D_t$.[7] It is reasonably expected that as the concentration of H_2O increases (i.e., the hydrogen bond formation is promoted),[5] the rotational and translational motions of H_2O in sc-CO_2 should be slowed down.[8] Hence, τ_r and $1/D_t$ will increase with c, which brings about a raise of $1/T_{1,\,dd}$ in both the intramolecular and intermolecular interactions. However, the observed concentration dependence was negative at 10 and 20 MPa.

The spin-rotation relaxation time ($T_{1,\,\mathrm{sr}}$) for a spherical top molecule under the extreme narrowing condition is given by[7, 9]

$$1/T_{1,\,\mathrm{sr}} = (2kT/\hbar^2)\, I_{\mathrm{av}}\, C_{\mathrm{eff}}^{\,2}\, \tau_J \qquad (2)$$

where I_{av} is the average moment of inertia, C_{eff} is the effective spin-rotation constant, and τ_J is the angular momentum correlation time, which corresponds to the average time between collisions resulting in angular momentum energy transfer. If I_{av} and C_{eff} are not very dependent on c at fixed pressure and temperature, $1/T_{1,\,\mathrm{sr}}(c)$ is simply proportional to $\tau_J(c)$. We expect that as c increases, the collisions between H_2O molecules become frequent in sc-CO_2, which can shorten the angular momentum correlation time, consequently, $1/T_{1,\,\mathrm{sr}}$ of H_2O molecules.

In order to verify that the spin-rotation interaction is the predominant mechanism, we carried out the isotope dilution (0.05 H_2O + 0.95 D_2O in mole fraction) experiments in sc-CO_2. If the dipole–dipole interactions contribute to $1/T_1^{\mathrm{obs}}$, $1/T_1^{\mathrm{obs}}$ should decrease because of smaller magnetogyric ratio of ^{2}D than that of ^{1}H. On the other hand, since the D substitution will not bring about the change in I_{av} and C_{eff} very much, $1/T_{1,\,\mathrm{sr}}$ is not significantly affected by the isotope dilution. In fact, Tsukahara et al.[10] recently demonstrated that ^{1}H relaxation times of normal and D_2O-diluted water were almost identical with each other above 523 K, where the spin-rotation interaction is predominant. $1/T_1^{\mathrm{obs}}$ of the D_2O-diluted water in sc-CO_2 is plotted against the total concentration[11] of water in Figure 1 (closed symbols). The values of $1/T_1^{\mathrm{obs}}$ of D_2O-diluted water were slightly larger than those of normal water. The slight increase of $1/T_1^{\mathrm{obs}}$ may be attributable to the isotope effect on $1/T_{1,\,\mathrm{sr}}$. This fact supports that T_1^{obs} can be almost regarded as $T_{1,\,\mathrm{sr}}$ at high c. Unfortunately, because of very low signal intensities, it is impossible to determine precisely T_1^{obs} of D_2O-diluted water at low c. However, as mentioned above, the contributions of the intramolecular and intermolecular dipole–dipole interactions to $1/T_1^{\mathrm{obs}}$ should decrease at low c. Thus, we expect that the relaxation mechanism remains the same as well at low c.

What does the change in $1/T_1^{\mathrm{obs}}$ of H_2O in sc-CO_2 indicate ? We measured the concentration dependence of ^{1}H chemical shift (δ) of H_2O in sc-CO_2, which showed a small monotonous linear increase with c ($\partial\delta/\partial c = (6.3 \pm 0.4) \times 10^{-4}\ \mathrm{mol^{-1}m^3}$ at 20 MPa).[5] At the present stage, we consider that the change in $1/T_1^{\mathrm{obs}}$ is mainly attributable to that in τ_J of H_2O molecules. The observed concentration dependence reflects a structural change in the hydrogen bonding between H_2O molecules in the solutions. It is very interesting that $1/T_1^{\mathrm{obs}}$ reaches a constant, which suggests that τ_J of H_2O molecules is no longer dependent on c. We are now in progress to measure $1/T_1^{\mathrm{obs}}$ of H_2O in CO_2 at different pressures to elucidate the solvent effect on the hydrogen bonding formation in the solutions.

The observed concentration dependence of $1/T_1^{\mathrm{obs}}$, which can be regarded as $1/T_{1,\,\mathrm{sr}}$, mainly reflects a change in τ_J of H_2O in sc-CO_2. Until now, there have been studies on τ_r of water, but little on τ_J in the solutions. We found that the angular momentum correlation time is a very sensitive probe to the hydrogen bond formation between H_2O molecules in sc-CO_2 solutions.

References and Notes

1 Only solubility data are available from R. Wiebe and V. L. Gaddy, *J. Am. Chem. Soc.*, **63**, 475 (1941); R. Weibe, *Chem. Rev.*, **29**, 475 (1941).

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6 Since a CO_2 molecule favorably has less magnetic-active nuclei in natural abundance, the intermolecular magnetic dipole–dipole interaction between the solute and solvent is negligible.

7 J. McConnell, in "The Theory of Nuclear Magnetic Relaxation in Liquids," Cambridge University Press, Cambridge (1987).

8 The τ_r and $1/D_t$ of solitary water in organic solvents are very sensitive to not only the macroscopic viscosity but also the short-ranged solute–solvent interactions as demonstrated by M. Nakahara and C. Wakai, *J. Chem. Phys.*, **97**, 4413 (1992) and *J. Chem. Phys.*, **106**, 7512 (1997). In the similar manner, we expect the motional slowdown of water molecules when the hydrogen bond formation is promoted.

9 As an approximation, we use Equation 2 for a non-spherical water molecule in accordance with the previous work of W. J. Lamb and J. Jonas, *J. Chem. Phys.*, **74**, 913 (1981). More rigorous treatment should be made for the quantitative analysis; see, for example, C. M. V. Taylor, S. Bai, C. L. Mayne, and D. M. Grant, *J. Phys. Chem. B*, **101**, 5652 (1997).

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11 No isotope effect on the solubility of water into carbon dioxide was assumed.