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Intramolecular and Intermolecular Hydrogen Bonds of 4-Hydroxy-4-methylpentan-2-one in Supercritical Xenon

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Infrared spectra of 4-hydroxy-4-methylpentan-2-one dissolved in supercritical xenon fluid have been measured at pressures in the 30–120 bar range and at 298 K. The overlapping OH stretching bands of the hydrogen-bond-free OH (ν_f), intramolecularly hydrogen-bonded OH (ν_{ib}), and intermolecularly hydrogen-bonded OH (ν_b) were resolved by least-squares fitting. The intensity of the ν_b band relative to the ν_{ib} band is largest at the lowest experimental pressure, where the solute concentration is only about 1 mM, and rapidly decreases with increasing pressure. This hydrogen-bonded complex may be a precursor of nucleation for solute precipitation. In the higher pressure range where the degree of the intermolecular hydrogen bonding is negligibly small, a logarithmic plot of the intensity ratio of the ν_f and ν_{ib} bands, A_f/A_{ib} , against pressure is remarkably nonlinear and its slope provides the partial molar volume change ΔV for the rotational isomerization as a function of pressure. The resulting value of ΔV reaches $-890 \text{ cm}^3 \text{ mol}^{-1}$ at 67 bar. This anomalously large change in volume is interpreted as a result of clustering of xenon about solute molecules. Frequency shift of the ν_{ib} band provides other evidence of the solvent clustering, which is shown to be consistent with the pressure dependence of $\ln(A_f/A_{ib})$.

Introduction

Solvation plays an important role in determining the conformation¹ of various molecules in the liquid state and is essential to understanding their physicochemical properties. Molecules with weak to moderate intramolecular hydrogen bonds are particularly interesting, because their conformation is easily influenced by solvation. Recently, we have studied the effect of pressure and temperature on the infrared spectrum of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) in dilute solutions.² This molecule exhibits an equilibrium between the intramolecular hydrogen-bonded (hereafter designated as HBd) and hydrogen-bond-free (hereafter designated as HBfree) conformers, as shown in Figure 1. We have found that the effect of solvation on the equilibrium is well explained by a dielectric continuum model combined with molecular mechanics calculations.² For a further molecular-level study of the solvation effect, supercritical fluid is an intriguing solvent. This paper's aim is to study the hydrogen bond of diacetone alcohol in supercritical xenon fluid by infrared spectroscopy.

Fluids at slightly supercritical temperatures are highly compressible and their physical properties (densities, dielectric constants, viscosities, diffusion constants, etc.) can be varied continuously from the gas to the liquid phase limits with modest changes in pressure.^{3,4} Moreover, with increasing densities, their dissolving power for various compounds is dramatically enhanced at around their critical densities.^{5–7} Because of these unique characteristics, supercritical fluids having critical temperatures in the vicinity of the ambient temperature, typified by carbon dioxide ($T_c = 304.2 \text{ K}$, $P_c = 7.38 \text{ MPa}$), have been widely used as solvents for extraction,^{8–11} as the mobile phase in chromatography,^{12–14} and as media for chemical reactions^{15–18} and syntheses.^{19–21}

Recently, molecular level structures and interactions in supercritical fluid solutions have been paid much attention. Eckert et al.²² observed remarkably large and negative solute partial molar volumes in supercritical solvents. This has been explained by local density augmentation of solvent molecules about the solutes as compared with the bulk solvent density. The local density augmentation, which is called solvent clustering, was shown

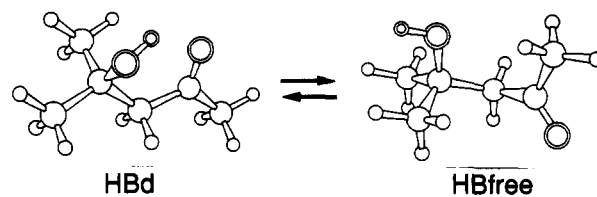


Figure 1. Rotational isomerization of the HBd and HBfree conformers of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol). ●, H(O); ○, H(C); ⊙, O; ○, C. Structures were obtained from molecular mechanics calculations.²

by Debenedetti²³ to be closely related to the solubility enhancement mentioned above. The concept of the solvent clustering or the local density augmentation has also been supported by theoretical studies with molecular dynamics simulation^{24,25} and the integral equation theory.²⁶

To understand the molecular level aspects of the solute–solvent and solute–solute interactions in the supercritical fluid solutions, spectroscopic measurements are particularly useful. Deviation of the observed frequencies of electronic^{27–33} or vibrational³⁴ transitions of solutes from theoretical predictions by dielectric continuum models is explained by local-field enhancement due to the solvent clustering. From these frequency deviations, Morita and Kajimoto³⁰ and Betts et al.³⁵ estimated solvation numbers or cluster sizes about solutes. Equilibria and kinetics of chemical reactions in the supercritical fluid solutions have been investigated by UV–vis absorption and emission,^{17,27,36–41} fluorescence,^{42,43} infrared absorption,^{44–48} and ESR spectroscopy.⁴⁹ Particularly intriguing properties are partial molar volume changes^{37,50} for isomerization of solute molecules and activation volumes^{18,45,49} of chemical reactions. The magnitudes of these properties become anomalously large in the vicinity of the solvent critical points as the above-mentioned partial molar volumes²² and related to differences in cluster size²³ between isomers or between reactants and activated intermediates.

In addition to the solvent clustering, very recently, enhancement of solute–solute interaction in the dilute supercritical fluid solutions has been suggested. Roberts et al.⁵¹ reported that the two-molecule reaction rate of triplet benzophenone photoreduction in supercritical carbon dioxide sharply increased with decreasing pressure toward the critical point of the solvent. The same

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behavior of the two-molecule reaction rate was observed by Combes et al.⁵² for the photodimerization of cyclohexenone in supercritical carbon dioxide. The enhancement of the solute-solute association has also been reported for a hydrogen-bonding system,⁴⁸ which is closely related to the present study and will be discussed in the later section. These experimental results are consistent with the theoretical calculation by Wu et al.²⁶ using the integral equation theory. Their calculated result showed evidence of solute-solute association in extremely dilute solution in supercritical fluid and of a sharp increase of the association rate with decreasing solvent density. On the other hand, Zagrobelny and Bright^{42,53,54} reported that the excimer formation of pyrene in supercritical carbon dioxide could be explained simply by a diffusion-controlled process without assuming any specific solute-solute interaction in their ground state. For the present, the concept of the solute-solute association in dilute supercritical fluid solutions is still an open question and further experimental studies are required. Whether the concept is useful or not is likely dependent on solute-solvent combinations and ranges of both solute concentration and solvent density.

Xenon, being completely transparent in the wide spectral range from UV to far-IR and being chemically inert, has usually been used as a low-temperature matrix⁵⁵ and a liquid solvent⁵⁶⁻⁵⁹ for spectroscopic studies. Recently, xenon has been also used as a supercritical solvent.^{16,34,40,60,61} Its critical point ($T_c = 289.8$ K, $P_c = 59.0$ bar) is in the easy range to manipulate and its moderate solvent power is fit for spectral measurements. In addition, xenon is a simple monatomic fluid and its interaction with solute molecules can be described by a simple potential, which is convenient for theoretical modeling. In this study, we have measured the infrared OH stretching absorption of diacetone alcohol in supercritical xenon and observed three component bands assigned to the HBfree and HBd conformers and the intermolecularly hydrogen-bonded complex. Obtaining their relative intensities as functions of pressure, we discuss the effect of solvation on the equilibrium between those species.

Experimental Method and Results

Xenon gas of 99.995% purity purchased from Hokusan and extra pure reagent grade diacetone alcohol from Nacalai Tesque were used as received. A schematic of the high-pressure cell used is shown in Figure 2. The cell body is made of stainless steel SUS 630 and the effective aperture for optical transmission is 6 mm. The windows are hyperpure silicon crystals of 10-mm diameter and 10-mm thickness and the optical path length for a sample is fixed at 8 mm. O-rings are used for pressure seal of the windows. Spectral measurements were performed by the use of a BOMEM DA3 Fourier-transform spectrometer with resolution of 2 cm^{-1} . First, a small amount of a sample (nonvolatile) was put in a small hole on the top of the sample plug, which was then attached to the bottom of the cell. Next, the cell was set in a stainless steel chamber, which was mounted on the sample compartment of the spectrometer. After evacuating the inside of the cell with a rotary pump, xenon fluid was gradually introduced into the cell with a compressor, and infrared transmission measurements were performed at each step of pressure in the 0–120 bar (± 0.5 bar) range at 298 K ($\pm 0.2\text{ K}$). Since the vapor pressure of diacetone alcohol is very low, absorption was not appreciable until the xenon pressure reached about 30 bar. Above this pressure, absorption of the sample grew rapidly with increasing pressure as shown in Figure 3. The integrated intensities of both the OH and CH stretching regions, which are plotted against pressure in Figure 4, increase at almost the same rate. Approximate solute concentrations are estimated by comparing the OH band intensities with that measured in a carbon disulfide solution of known concentration.² The results are in the range $1.1\text{--}15\text{ mM}$ or 7×10^{-4} to 1×10^{-3} in mole fraction, where the densities of xenon fluid reported by Michels et al.⁶² were

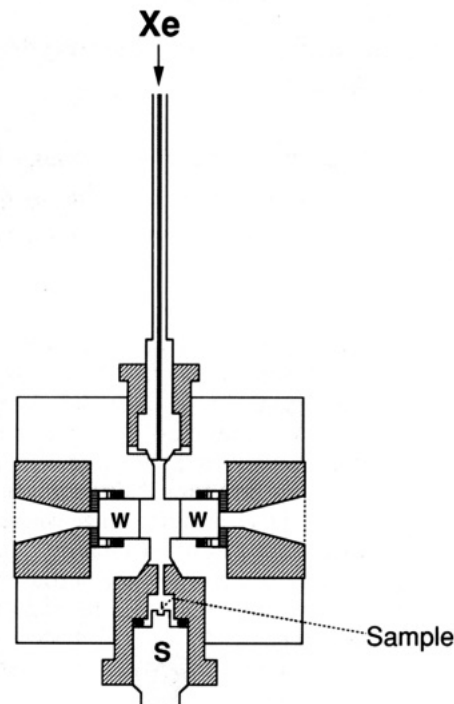


Figure 2. Schematic of the high-pressure cell. W, Si windows (10-mm diameter and 10-mm thickness); S, Sample plug.

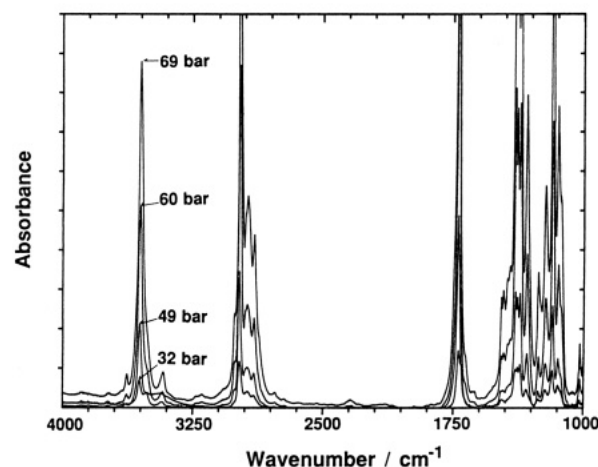


Figure 3. Infrared absorption of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) dissolved in xenon at various pressures and 298 K .

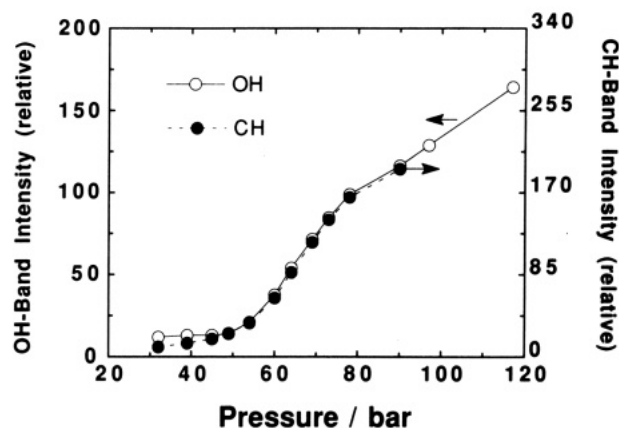


Figure 4. Plots of absorption intensity vs pressure for the OH and CH stretching bands of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) in supercritical xenon.

used. Figure 5 compares the OH stretching bands measured in different phases. The gas-phase spectrum was measured with a gas cell of 10-m path length. Obviously the supercritical xenon

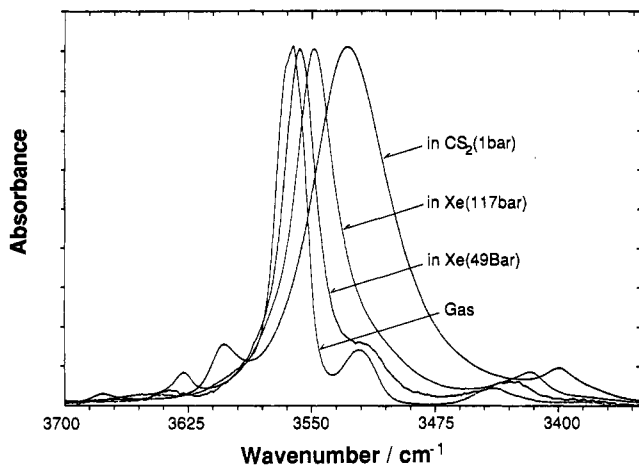


Figure 5. OH stretching bands of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) in various phases. The intensities are normalized to constant peak maxima.

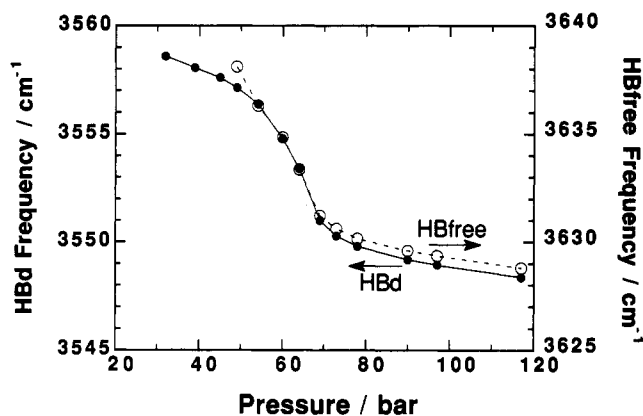


Figure 6. Plots of peak frequency vs. pressure for the ν_{ib} and ν_r bands of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) in supercritical xenon.

fluid provides a solvent that is able to bridge continuously the gap between the gas-phase and ordinary solutions.

Figure 5 shows four bands at about 3620, 3550, 3520, and 3420 cm^{-1} . The first two bands are assigned to the HBfree and HBd OH stretchings, ν_r and ν_{ib} , respectively, and the last one to the overtone of the C=O stretching. The peak at 3520 cm^{-1} is clearly seen only in the gas phase and in low-pressure xenon but merges into the ν_{ib} band in high-pressure xenon and in carbon disulfide, causing the asymmetric band profile. This band may be assigned to a hot band transition from an excited states of a low-frequency mode, which heavily couples with the OH stretching of the HBd conformer.² The overlap of these bands was resolved by least-squares fitting with a computer. Each of the HBfree OH and the overtone bands was represented by a single Lorentzian function, while the HBd OH band, which includes the 3550 and 3520 cm^{-1} bands, was represented by a sum of two Gaussian functions. The peak frequencies of the ν_r and ν_{ib} bands are plotted against pressure in Figure 6 and the logarithmic plots of the intensity ratio of the ν_r and ν_{ib} bands, A_r/A_{ib} , are shown in Figure 7. These results are discussed in the next section.

Spectra at low xenon pressures shown in Figure 8 exhibit a striking feature. The broad band at around 3430 cm^{-1} is assigned to the intermolecularly hydrogen-bonded OH stretching, ν_b . The intensity of the ν_b band relative to the ν_{ib} band decreases rapidly with increasing pressure and decays almost completely at pressures above 49 bar, while a small band of the C=O overtone remains. The corresponding change is observed in the fundamental C=O stretching region shown in Figure 9. A peak at 1720 cm^{-1} and a shoulder at about 1705 cm^{-1} are assigned to the intramolecularly and intermolecularly hydrogen-bonded C=O stretchings, re-

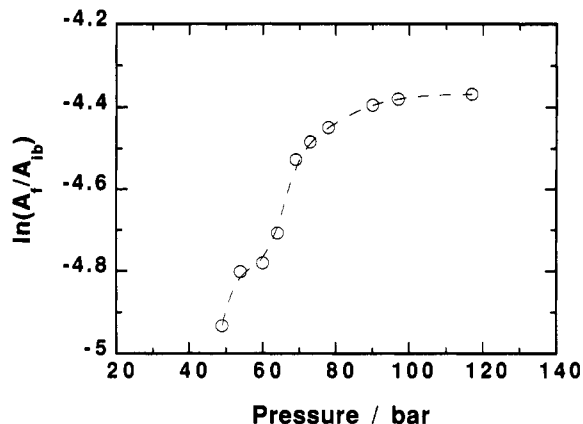


Figure 7. Logarithmic plot of the intensity ratio of the ν_r and ν_{ib} bands against pressure.

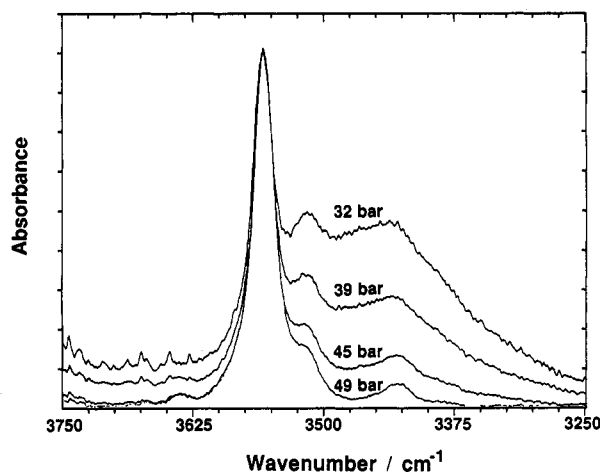


Figure 8. OH stretching bands of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) in xenon at low pressures. The intensities are normalized to constant peak maxima.

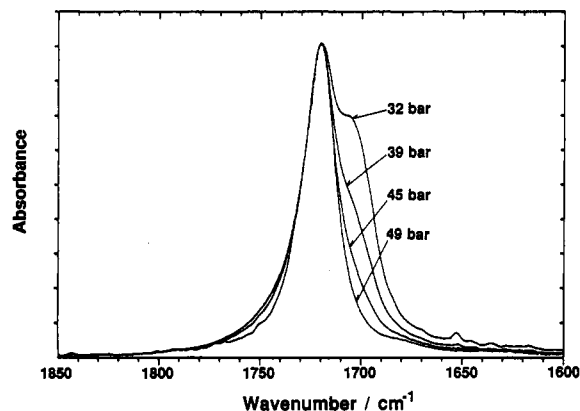


Figure 9. C=O stretching bands of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) in xenon at low pressures. The intensities are normalized to constant peak maxima.

spectively. Since the 1705- cm^{-1} band decays at nearly the same rate as the ν_b band, the intermolecular hydrogen bonding is considered to be between the OH and C=O groups.

The hydrogen-bonded complex would result from condensation on the windows if the liquid phase migrates via the vapor phase. However, spectral observation suggested that this is not the case. Several successive scans at each step of pressure showed that the absorption reached the equilibrium within a few minutes after pressurizing and changed little afterward. If the liquid-phase migration occurred, the ν_b band intensity would increase gradually for quite a long time at a constant pressure.

Discussion

Hydrogen-Bonded Complex. The spectrum at low pressures indicates that the intermolecular hydrogen bonding occurs in low-density xenon, where the solute concentration is on the order of 1 mM. The hydrogen-bonded complex decays rapidly with increasing pressure and can be observed only in the region below 49 bar. In the range 32–49 bar, which is well below the critical pressure of xenon, the solubility increases slightly as seen in Figure 4 and the mole fraction of the solute remains almost constant at about 7×10^{-4} . This is contrary to the well-known fact that, in ordinary solutions, the proportion of hydrogen-bonded complex increases with increasing concentration. The hydrogen-bonded complex found at the low xenon pressures, where the solubility is very small, may be a precursor of the nucleation for solute precipitation. This fact seems to be related to the solute–solute association mentioned before. However, the pressure ranges where the solute–solute association has been found^{51,52} are immediately above the solvent critical pressures, while the pressures for finding the hydrogen-bonded complex in the present study are obviously below the critical pressure of xenon. This is probably due to differences in strength of the intermolecular interactions and in solubility range.

The present result bears some resemblance to recent observations on the intermolecular hydrogen bonding in supercritical fluid solvents. Fulton et al.⁴⁴ measured the infrared OD stretching bands of methyl alcohol-*d* in supercritical ethane and found that the degree of solute–solute intermolecular hydrogen bonding decreased as ethane pressure increased from 30 to 100 bar. This phenomenon was explained by a decrease in the mole fraction of alcohol with increasing pressure, because their experiment was done at a constant solute molarity, 25 mM. Very recently, Gupta et al.⁴⁸ reported a FTIR study of the hydrogen bonding between methanol and triethylamine in supercritical sulfur hexafluoride. They found that the proportion of the hydrogen-bonded complex decreased with increasing pressure in the near-critical region of the solution and concluded that the donor and acceptor was destabilized more than the complex as the solvation was reduced.

These experimental results provide an important clue to the solvation effect on the hydrogen bonding and show usefulness of the supercritical fluid solvents.

Rotational Isomerization. At pressures above 49 bar, the hydrogen-bonded complex decays completely and there exist only monomers. Then the intensity ratio A_f/A_{ib} as a function pressure gives knowledge about the partial molar volume change associated with the rotational isomerization. As shown in Figure 7, the logarithm of the intensity ratio is remarkably nonlinear to pressure. This is distinctly different from the same kind of plot for ordinary solutions, which is approximately linear, and its slope gives the partial molar volume change for the isomerization by

$$\Delta V = -RT \frac{\partial \ln(A_f/A_{ib})}{\partial P} \quad (1)$$

The nonlinear plot in Figure 7 indicates that ΔV is considerably pressure-dependent near the critical point of xenon. The calculated values of ΔV are plotted against the pressure in Figure 10a. It reaches $-890 \text{ cm}^3 \text{ mol}^{-1}$ at 67 bar where the compressibility of xenon fluid has a maximum at the experimental temperature, 298 K. This anomalously large negative value of ΔV is 2 orders of magnitude larger than those measured for carbon tetrachloride and carbon disulfide solutions at room temperature, -4.0 and $-3.9 \text{ cm}^3 \text{ mol}^{-1}$,² respectively.

Similar large changes in the partial molar volumes have been reported for a few systems. Johnston and co-workers measured very negative partial molar volume changes for the reduction of I_2 to I^- in supercritical water⁵⁰ and for the tautomerization of 2-hydroxypyridine to 2-pyridone in supercritical propane and supercritical 1,1-difluoroethane.³⁷ Ikushima et al.⁴⁵ reported a

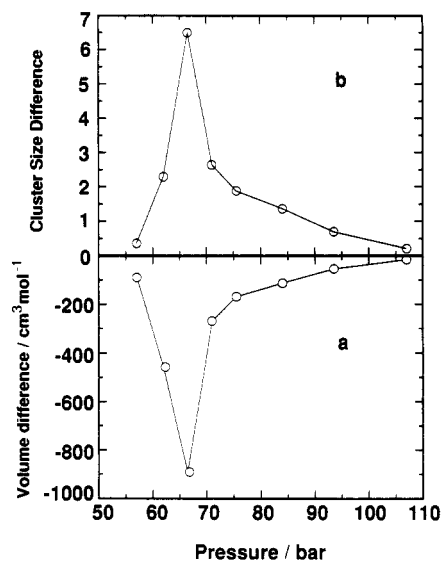


Figure 10. Pressure dependences of the partial molar volume change for the rotational isomerization (a) and the cluster size difference (b) between the HBfree and HBd conformers of 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) in supercritical xenon.

large negative activation volume of the Diels–Alder reaction between isoprene and methyl acrylate in supercritical carbon dioxide.

These anomalously large volume changes are interpreted as a result of local density augmentation, or clustering, of solvent molecules around the solute molecules. The state of the clustering at the near-critical region of solvents is very sensitive to solute–solvent interaction,⁶³ and even a small difference in the interaction causes a rather anomalously large difference in the partial molar volume among isomers or species involved in chemical reactions. Therefore, the supercritical solvents will be particularly useful to a detailed study of the intermolecular interactions that control the chemical processes in solutions.

On the basis of a fluctuation theory of solutions, Debenedetti²³ has shown that the partial molar volume of an infinitely dilute solute is related to the cluster size that is defined as the excess number of solvent molecules surrounding the solute molecule with respect to a uniform distribution at the bulk density of the solvents. The cluster size, ξ_c , is given by

$$\xi_c = \rho^0 (k_B T K_T - \overline{V_s^\infty}) \quad (2)$$

where ρ^0 is the bulk solvent density, k_B Boltzmann's constant, K_T the isothermal compressibility of the pure solvent, and $\overline{V_s^\infty}$ the partial molar volume of the infinitely dilute solute. Then, the partial molar volume change for isomerization gives the difference in the cluster size between isomers,

$$\Delta \xi_c = -\rho^0 \Delta \overline{V_s^\infty} \quad (3)$$

The cluster size differences calculated from the experimental $\Delta \overline{V_s^\infty}$ are plotted in Figure 10b. It is found that the average number of xenons surrounding the HBfree conformer is 6.5 more than that of the HBd conformer at 67 bar and 298 K.

Frequency Shift. The effect of the clustering is also found in the pressure dependence of the ν_{ib} band frequency, which is plotted in Figure 11 against $(\epsilon - 1)/(2\epsilon + 1)$. Here ϵ is the dielectric constant of xenon and its value at various pressures are estimated from the experimental values of the density ρ ⁶² and the Lorentz–Lorenz function of xenon, $(\epsilon - 1)/\{\rho(\epsilon + 2)\} = 0.080158 \text{ cm}^3 \text{ g}^{-1}$.⁶⁴

The gas-to-solution frequency shift of a dilute solute in an ordinary nonpolar solvent is well described by a reaction-field

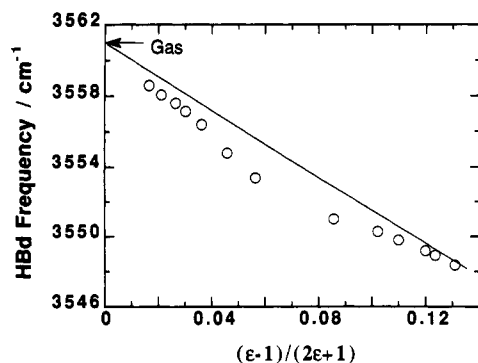


Figure 11. Plot of the ν_{ib} band frequency against $(\epsilon - 1)/(2\epsilon + 1)$, where ϵ is the dielectric constant of pure xenon.

effect and approximately given by⁶⁵

$$\nu_s - \nu_0 = -k \frac{(\epsilon - 1)}{(2\epsilon + 1)} \quad (4)$$

where, ν_s and ν_0 are the solution and gas-phase frequencies, respectively, ϵ is the dielectric constant of the pure solvent, and k is a proportional constant. Usually, k is treated as an empirical parameter, because most of the intramolecular and intermolecular potential parameters that are required for calculating k are difficult to estimate.

The relationship of eq 4 is represented by a straight line in Figure 11 on the assumption that the observed frequency approaches this line at the high-pressure limit where the solvent density around a solute molecule will be close to the bulk solvent density as in ordinary solutions. The observed frequency plots are obviously below the straight line. This means that the vibrational frequency of the solute shifts farther than expected from the pure xenon density at the same pressure and indicates a local density augmentation near the solute molecules. The deviation is maximum at around $(\epsilon - 1)/(2\epsilon + 1) = 0.07$, where the xenon pressure is 67 bar, being consistent with the pressure for the most negative value of ΔV . This is interpreted as another evidence of the solvent clustering, by which the "effective dielectric constant" in the solvation area is distinctly larger than the bulk dielectric constant.

Effective Dielectric Constant. The concept of the "effective dielectric constant" can be tested by considering the pressure dependence of $\ln(A_f/A_{ib})$ on the basis of a dielectric model. The equilibrium constant K between the HBfree and HBd conformers is given by

$$K = \frac{A_f I_{ib}}{A_{ib} I_f} \quad (5)$$

where I_f and I_{ib} denote the molar integrated intensities. Following a dielectric theory of the solvation energy, K is given by^{1,2}

$$RT \ln K = \frac{\epsilon - 1}{2\epsilon + 1} \left\{ \frac{\mu_f^2 - \mu_{ib}^2}{(1 - \alpha f)a^3} + \frac{3(2\epsilon + 1)(\eta_f^2 - \eta_{ib}^2)}{2(3\epsilon + 2)a^5} \right\} \quad (6)$$

where μ and η are the dipole moment and the anisotropic rotational invariant of the quadrupole, respectively, a and α are the molecular radius and polarizability, and $f = (2\epsilon - 2)/(2\epsilon + 1)a^3$ is a reaction-field factor. Using the Lorentz-Lorenz equation, the product αf is given by

$$\alpha f = \frac{n_D^2 - 1}{n_D^2 + 2} \frac{2\epsilon - 2}{2\epsilon + 1} \quad (7)$$

where n_D is the refractive index of the solute for the sodium D line. Substitution of eq 5 into eq 6 gives the following relationship:

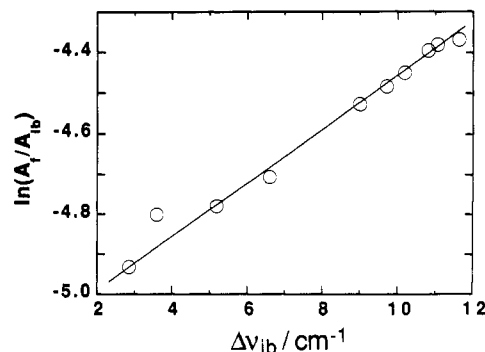


Figure 12. Correlation between the logarithm of the intensity ratio, $\ln(A_f/A_{ib})$, and the frequency shift, $\Delta\nu_{ib}$.

$$\ln\left(\frac{A_f}{A_{ib}}\right) = \frac{1}{RT} \frac{\epsilon - 1}{2\epsilon + 1} \left\{ \frac{\mu_f^2 - \mu_{ib}^2}{(1 - \alpha f)a^3} + \frac{3(2\epsilon + 1)(\eta_f^2 - \eta_{ib}^2)}{2(3\epsilon + 2)a^5} \right\} + \ln\left(\frac{I_f}{I_{ib}}\right) \quad (8)$$

The molar integrated intensities, I_f and I_{ib} , depend on temperature and pressure due mainly to change in the internal-field strength,⁶⁶ which depends on the solvent density. However, their ratio I_f/I_{ib} will be approximately independent of pressure as observed for solutions in ordinary solvents.⁶⁶ Therefore, the pressure dependence of the right-hand side of eq 8 arises from ϵ . As the pressure increases from 30 to 120 bar, the factor $(\epsilon - 1)/(2\epsilon + 1)$ increases 6.5 times, while the values of $(1 - \alpha f)^{-1}$ and $(6\epsilon + 3)/(6\epsilon + 4)$ increase only 1.06 and 1.02 times, respectively. Therefore, eq 8 is approximately reduced to

$$\ln\left(\frac{A_f}{A_{ib}}\right) - C_0 = C_1 \frac{\epsilon - 1}{2\epsilon + 1} \quad (9)$$

where C_0 and C_1 are independent of pressure. From eqs 4 and 9, we obtain

$$\ln\left(\frac{A_f}{A_{ib}}\right) = C_0 + \frac{C_1}{k} \Delta\nu_{ib} \quad (10)$$

where $\Delta\nu_{ib} = \nu_0 - \nu_s$. A linear plot for experimental $\ln(A_f/A_{ib})$ vs $\Delta\nu_{ib}$ shown in Figure 12 is consistent with the above relationship. This indicates that the concept of the effective dielectric constant is useful for characterizing the solvent cluster. By comparing the effective and the bulk dielectric constants, the density of xenon around the solute is estimated to be 1.5 times the bulk density at about 67 bar. Here, we have allowed for the fact that the value of the Lorentz-Lorenz function is independent of density to a very good approximation.⁶⁴

Conclusion

It has been shown that supercritical xenon is a useful solvent for a spectroscopic study of the solvation effect on intermolecular and intramolecular hydrogen bonding. Being completely transparent in the wide spectral region and having its critical point in the easy range to manipulate, supercritical xenon provides a unique solvent that fills continuously the gap between the gas-phase and ordinary solutions. The hydrogen-bonded complex of diacetone alcohol found only in low pressure xenon, where the solubility is very low, may be a precursor of solute nucleation and provides an important clue to role of solvation in the dissolving process of hydrogen-bonded compounds.

Partial molar volume change of the rotational isomerization of diacetone alcohol, which is associated with breaking of the intramolecular hydrogen bond, reaches $-890 \text{ cm}^3 \text{ mol}^{-1}$ at 67 bar, where xenon compressibility has a maximum at an experimental temperature of 298 K. This result indicates that the solvent density around the HBfree conformer is distinctly larger

than that around the HBd conformer near the critical density of xenon. This difference in solvent clustering is important information about solute-solvent interaction, which is different, even if slightly, between the two conformers. It is then possible to study in detail the correlation between molecular conformation and interaction.

Pressure dependences of both the OH stretching frequency and the conformational equilibrium are consistently explained by the concept of the effective dielectric constant in the solvation area.

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