Ab Initio Study of Proton Chemical Shift in Supercritical Methanol Using Gas-Phase Approximation

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Chemical shifts of the OH proton in supercritical methanol referenced to the methyl proton of methanol monomer have been estimated theoretically using the ab initio molecular orbital (MO) method. The degree of dissociation from hydrogen-bonded methanol clusters to monomers calculated using the CCSD(T)/6-31+G(d)//MP2(frozen-core)/6-31+G(d) level of theory indicates that supercritical methanol is comprised of 89% monomer and 10% cyclic tetramer plus ∼1% dimer at the critical point ($T_c = 512.6$ K; $P_c = 8.09$ MPa). The predominant existence of the cyclic tetramers rather than the dimers in supercritical methanol is in contrast to previous theoretical results for supercritical water that indicate the composition of, except for 80% monomer, 20% dimer with little existence of a larger size of clusters at the critical point ($T_c = 647.1$ K; $P_c = 22.06$ MPa). It is also found that a significant fluctuation of the composition of methanol should be caused by a greater change in the degree of dissociation of the cyclic tetramer near the critical point. On the basis of the above supercritical methanol composition, the chemical shift of the OH proton is determined to be −2.00 ppm at the MP2(frozen-core)/6-31+G(d)//MP2(frozen-core)/6-31+G(d) level of theory, which excellently reproduces the recent NMR experimental results.

I. Introduction

Supercritical fluids have been an attractive subject for study because of the expectation of their potential abilities for environmental and industrial applications.[1−3] The motivation of this subject seems to be mainly inclined toward environmental science and technology. We think that a better understanding of the microscopic structures at the atomic level of supercritical fluids can not only make good use of their unique properties of both gaslike and liquidlike characteristics but also promote development of the above applications.

Methanol is one of the simplest self-association polar solvents, which forms a hydrogen-bonded network structure due to its OH group. The critical point,[4] CP ($T_c = 512.6$ K; $P_c = 8.09$ MPa) of methanol is much easier to obtain than the CP ($T_c = 647.1$ K; $P_c = 22.06$ MPa) of water, indicating that methanol has weaker hydrogen bonds and that its critical conditions should become more advantageous for industrial processes compared to water. It seems to be confirmed that the extent of hydrogen bonds in methanol decreases in the condition of higher temperature and lower density according to the measurements,[5−7] such as the case of water,[8−10] though most of the studies have not dealt with the supercritical state and there is still little information about the intermolecular interaction in this state. However, recent experimental studies, especially NMR[11,12] and neutron diffraction,[13] indicate the destruction of about 70−90% of the hydrogen bonds and the predominant existence of monomers and small sizes (ca. <5 molecules) of oligomers containing cyclic-type structures in supercritical methanol. On the other hand, there are simpler compositions of monomers and dimers in supercritical water at the CP[14−16] compared to supercritical methanol. Considering the smaller dielectric constants of $\epsilon \approx 5-6$ for methanol[17,18] and 5 for water[19] at the CP compared to $\epsilon \approx 32$ for the former and 80 for the latter in the normal state, it is evident that there is a significant breakdown of the hydrogen bonds in these hydrogen-bonded liquids in the supercritical state. We have been interested in the influence of hydrogen bonding on specific chemical reactions in supercritical water and methanol. In the previous theoretical study for the noncatalytic Beckmann rearrangement and the hydrolysis of cyclohexanone-oxime in subcritical and supercritical water, we found that the hydrogen bonds between the nitrogen (or oxygen) atom of cyclohexanone−oxime and water are an important key in the initial reaction step and that the activation energies of the hydrolysis are very sensitive to the dielectric constant reflecting the extent of the hydrogen bonds.[20]

Molecular orbital (MO) theory can well describe the hydrogen bonding formed by the interaction between the OH hydrogen of an electron donor and the proximate OH oxygen of an electron acceptor in the gas phase. However, few ab initio MO calculations, except for several studies aimed at setting up a two-body intermolecular potential for the molecular dynamics (MD) or Monte Carlo (MC) simulations, have been conducted for investigating the hydrogen bonding in supercritical fluids. At first sight, each methanol molecule in the supercritical state might be thought to have a quite different electronic structure from that in the normal state; the electronic structure should be quite similar to that of an isolated methanol molecule due to its low density of 0.27 g/cm^3 at the CP. Experimental[21] and

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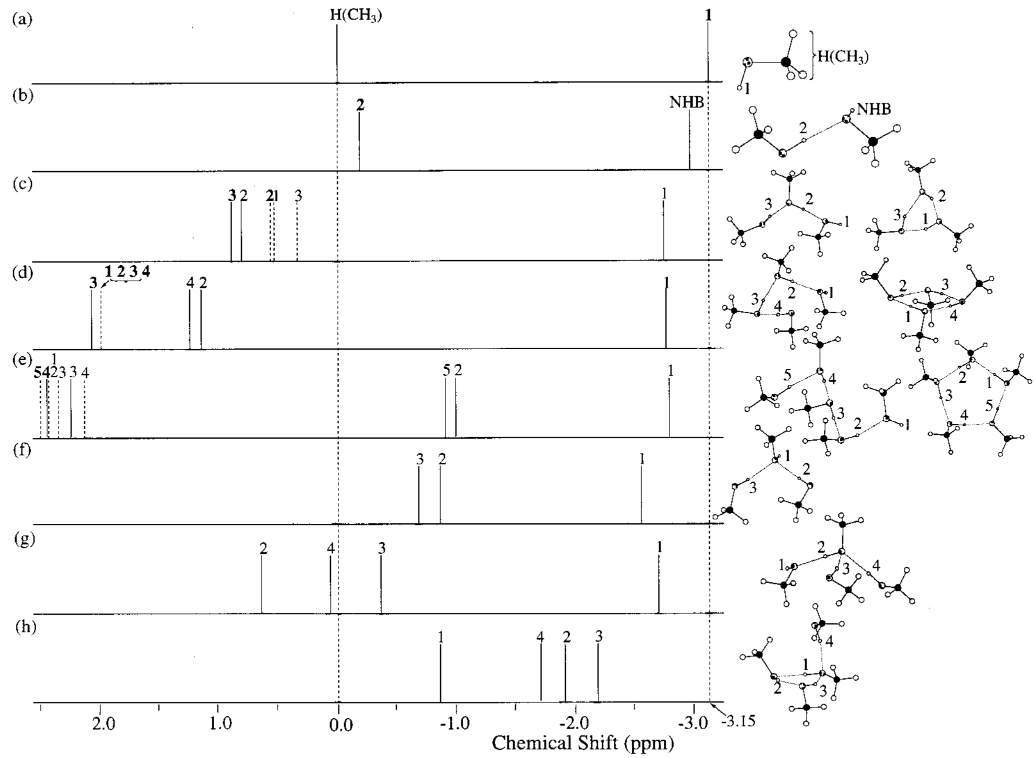

Figure 1. Stick diagram of the calculated chemical shifts of the OH proton of the methanol clusters: (a) monomer; (b) chain-dimer; (c) chain and cyclic-trimer; (d) chain & cyclic-tetramer; (e) chain and cyclic-pentamer; (f) branched-chain trimer; (g) branched-chain tetramer; (h) branched-cyclic tetramer. The chemical shift is referenced to the averaged values of the CH_3 protons of the monomer. The numbering on the chemical shifts corresponds to the OH proton numbering in each optimal methanol cluster in the insert. The dashed stick in panels c−e represents the chemical shifts of each cyclic cluster.

theoretical[22] studies on hydrogen-bonded methanol clusters have mostly been concentrated on the molecular structures, binding-energies, and vibrational frequencies, etc., of the clusters in the gas phase, such as water clusters;[23,24] there is little work on the ^{1}H NMR chemical shifts in water and methanol. We have reported in a short communication[25] that the cluster model under the gas phase approximation can reproduce well the NMR chemical shifts of the hydrogen-bonded proton in supercritical water. We thus carried out a theoretical NMR study using hydrogen-bonded methanol clusters prior to a study on chemical reactions in supercritical methanol. Methanol clusters have much simpler structures than water clusters due to contributing only one hydrogen to hydrogen bonding in contrast to water with two hydrogens.

We therefore theoretically estimated the chemical shifts at the CP on the basis of the degree of dissociation from the hydrogen-bonded methanol clusters to monomers in supercritical methanol, as in the previous study of supercritical water. We will discuss the calculated results of methanol in comparison with those of water.

II. Computational Methods

All the calculations were carried out with the GAUSSIAN 98 ab initio program package.[26] The magnetic shielding constant (in ppm) of the OH protons in the methanol monomer and clusters were calculated using the MP2(frozen-core)/6-31+G(d)//MP2(frozen-core)/6-31+G(d) levels with the gauge-independent atomic orbital (GIAO) method.[27−31] The previous calculations of the magnetic shielding constant of the protons for water clusters at the MP2 level of theory could better reproduce the experimental data compared to the HF and B3LYP level of theories with the same basis set.[25] The OH chemical shifts in the methanol clusters are referenced to the averaged value of the magnetic shielding constants of the methyl protons in the monomer. The degree of dissociation from each hydrogen-bonded methanol cluster to the monomers were estimated using the total energies of the CCSD(T)/6-31+G(d)//MP2(frozen-core)/6-31+G(d) level of theory with the enthalpy corrections and entropy at the MP2 level; an empirical scale factor of 0.94[32] is used for the calculations of these thermochemical properties. The calculated enthalpy and entropy consist of the translational, rotational and vibrational terms. All the optimized geometries, except for the size of clusters greater than the tetramer, corresponding to local minima were found to have real frequencies. A Silicon Graphics Octane R12000 workstation was used for the calculations in this study.

III. Results and Discussion

A. Structures and Stabilities of Methanol Clusters. The optimal hydrogen-bonded methanol clusters with the chain, cyclic, and branched-chain (or cyclic) structures are shown as inserts in Figure 1. We have checked the validity of the optimal structures and binding energy (E_b) for the present methanol clusters in comparison with those from the other theoretical calculations and experimental results.[22,33−37] The geometrical parameters, except for the branched clusters, and E_b are summarized in Table 1 and the right-hand side in Table 2, respectively; the E_b for the $(CH_3OH)_n$ clusters is defined as follows:

$$E_b = nE(\text{monomer}) - E(n\text{-mer}) \qquad (1)$$

For the binding energies, D_e denotes the electronic energy differences, whereas D_0 includes the zero-point energy corrections (ZPE). We found that the calculated geometries are in good agreement with the previous results at the B3LYP/6-

TABLE 1: Optimal Geometries of Methanol Clusters along with the Other Theoretical Results and Experimental Data[a]

	R(O−O), (Å)					δ(O···H−O), (deg)			
	this work		DFT[b]			this work		DFT[b]	
species	chain	cyclic	chain	cyclic	expt.[c]	chain	cyclic	chain	cyclic
$(CH_3OH)_2$	2.860		2.862		2.98	175.0		174.2	
$(CH_3OH)_3$	2.796	2.774	2.797	2.763		166.8	150.4	167.1	150.4
$(CH_3OH)_4$	2.769	2.738	2.769	2.737		169.0	168.3	172.1	168.4
$(CH_3OH)_5$	2.759	2.725		2.723		168.3	175.9		176.7
$(CH_3OH)_6$	2.751	2.717				167.7	176.8		

[a] Averaged values except for the dimer. [b] From ref 22; B3LYP/6-31+G(d) level. [c] From ref 33.

TABLE 2: Calculated Degree of Dissociation α, the Changes in Enthalpy Δ*H* (kcal/mol) and Entropy Δ*S* (cal/(mol K)),[a] and Binding Energy E_b (kcal/mol)[b] from Each Methanol Cluster to Monomers along with Experimental Data

		512.6 K					298.15 K					373 K (expt.)			
		ΔH	8.09 MPa		0.1 MPa		ΔH	8.09 MPa		0.1 MPa		ΔH	ΔS	E_b, D_0 (D_e)	
species	structure		α	ΔP	α	ΔS_{P_0}		α	ΔP	α	ΔS_{P_0}			this work[c]	DFT[d]
$(CH_3OH)_2$	chain	5.2	0.769	13.6	0.996	22.3	5.8	0.167	15.2	0.834	23.9	3.5[e]	17.4[e]	5.9 (7.5)	4.82 (6.28)
$(CH_3OH)_3$	chain	13.5	0.951	34.3	1.000	51.7	14.7	0.047	37.4	0.852	54.9			14.8 (18.1)	11.88 (14.94)
	cyclic	16.8	0.898	39.0	1.000	56.4	17.8	0.016	41.7	0.368	59.1	12.5[f]	44.2[f]	17.6 (21.5)	12.10 (18.40)
	branched -chain	9.7	0.998	31.5	1.000	57.6	11.1	0.276	34.9	0.999	52.3			11.4 (14.3)	8.44 (11.22)
$(CH_3OH)_4$	chain	22.7	0.992	56.6	1.000	82.8	24.5	0.018	61.2	0.794	87.3			24.5 (29.6)	19.33 (24.02)
	cyclic	30.5	0.662	62.9	1.000	89.0	32.0	0.001	66.6	0.043	92.7	24.2[g]	81.3[g]	31.5 (37.5)	27.19 (32.82)
	branched -chain	19.8	0.997	52.7	1.000	78.9	21.8	0.038	57.7	0.982	83.8			22.1 (26.8)	16.75 (21.08)
	branched -cyclic	23.7	0.997	60.8	1.000	86.9	25.5	0.020	65.2	0.848	91.3			25.3 (30.7)	20.02 (24.53)

[a] ΔS_P and ΔS_{P_0} are used in eq 5. [b] Defined in eq 1. [c] CCSD(T)/6-31+G(d)//MP2/6-31+G(d) level. [d] From ref 22; B3LYP/6-31+G(d) level. [e] From ref 35. [f] From ref 36. [g] From ref 37.

31+G(d) level of calculations.[22] It can be seen in Table 1 that the averaged distances of O−O decrease with the increasing size of both chain and cyclic clusters, indicating the stronger interaction between methanol molecules in larger size clusters. The similarity in characteristics can be seen in the cyclic water clusters in the previous calculations.[25] There is a large nonlinearity of the O−H···O bonds in the cyclic trimer compared to the other clusters, as also seen with the cyclic water trimer. We found that the cyclic clusters are a rather stable species than the others in each cluster size. We could not calculate D_0 for $n \geq 5$ and the chemical shifts for $n = 6$ due to significant computational costs at the present level of theory. However, as above-mentioned, the maximum cluster size n is less than about 5 methanol molecules at the supercritical state according to the measurements.[12,13] We then think it sufficient to examine the cluster size of $n \leq 4$ in Table 2. Although the E_b shows somewhat larger values compared to the previous results of calculations,[22] we think that the present level provides valid optimal structures and the E_b, on the whole because no change is seen in the order of the stability of the clusters in each size between the two level of calculations in Table 2.

B. Degree of Dissociation of Methanol Clusters. If the n-mer cluster-monomer equilibrium of dissociation is represented as

$$(CH_3OH)_n \leftrightarrows nCH_3OH \tag{2}$$

we can write the mole fractions without dependence on the nonzero initial concentration of the n-mer cluster using the degree of dissociation α from the n-mer cluster to the monomers as follows:

$$n\text{-mer cluster:} \quad (1 - \alpha)/(1 + (n - 1)\alpha) \tag{3}$$

$$\text{monomer:} \quad (n\alpha)/(1 + (n - 1)\alpha) \tag{4}$$

The pressure equilibrium constant, K_P, can be expressed using eqs 3 and 4 as follows:

$$K_P = \frac{(n\alpha)^n}{[1 + (n - 1)\alpha]^{n-1}(1 - \alpha)}\left(\frac{P}{P_0}\right)^{n-1} = \exp\left[-\frac{\Delta H - T\Delta S_P}{RT}\right]\left(\frac{P}{P_0}\right)^{n-1} = \exp\left[-\frac{\Delta H - T\Delta S_{P_0}}{RT}\right] \tag{5}$$

where P is pressure in atm units, P_0 is the standard pressure of 1 atm, T is temperature, R is the gas constant, and ΔH and ΔS_P (or ΔS_{P_0}) are the changes in enthalpy and entropy (see Table 2), respectively.[38] Because the degree of dissociation cannot solve the case of two or more components with the initial concentrations, K_P then represents the n-mer cluster-monomer equilibrium of dissociation under the zero initial concentration of the monomer. The degree of dissociation, $\alpha = 1.0$, represents the perfect dissociation from the n-mer cluster to the monomers.

The degree of dissociation from each n-mer cluster to monomers and the above thermochemical parameters for certain combinations of temperature and pressure are summarized in Table 2 along with the experimental data.[35−37] It can be seen in Table 2 that in the normal state (NS: 298.15 K; 0.10 MPa), the cyclic tetramer has the smallest degree of dissociation of all the present clusters. The larger-size cyclic clusters show a smaller degree of dissociation compared to that from the corresponding size of the chain and branched clusters, indicating that the hydrogen-bonded network structure, especially that formed by the larger size cyclic clusters, is more energetically favorable at NS. For the conditions of 298.15 K and 8.09 MPa, all the clusters have a smaller degree of dissociation due to the larger gain in entropy in the clusters than that in the monomer at high pressure. However, the dimer and branched-chain trimer show a somewhat larger degree of dissociation compared to other clusters. Under the conditions of 512.6 K and 0.10 MPa, namely, a high-temperature gas, it is quite natural that all the clusters dissociate into monomers. Next, at the CP of 512.6 K and 8.09 MPa, the chain and branched clusters, except for the dimer and the cyclic tetramer, should easily dissociate into monomers.

Contrary to expectations, the dimer and especially the cyclic tetramer show, respectively, smaller degrees of dissociation of 77% and 66%, in comparison with more than about 90% for the other *n*-mer clusters at the CP. The diagram of the degree of dissociation from the dimer and the cyclic tetramer to the monomers for the wide range of temperature and pressure containing the CP are shown in panels a and b, respectively, of Figure 2. It is natural to note that the degrees of dissociation in both the dimer and the cyclic tetramer in the supercritical state show smaller values for temperatures higher than the critical temperature at constant pressure and larger values for pressures higher than the critical pressure at constant temperature. Experimental results also suggested that the extent of hydrogen bonds in methanol[11,39] decreases with decreasing pressure in the region above T_c. It can be seen in Figure 2b that there is a drastic change in the degree of dissociation of the cyclic tetramer in the subcritical and supercritical states. On the other hand, there is a milder change in the degree of dissociation of the dimer in those states. It is expected that a larger fluctuation of the composition of methanol near the CP should be caused by a greater change in the degree of dissociation of the cyclic tetramer compared to the dimer. For this reason, it will then be difficult to experimentally determine the composition in supercritical methanol. Indeed, the recent measurements have remained uncertain about the structures of the small size of oligomers in the supercritical state. On the other hand, for supercritical water only two species exist, monomers and dimers predominante by measurements, which was supported by our previous theoretical results that show a smaller degree of dissociation of 66% for the water dimer compared to that of more than ca. 90% for the *n*-mer cyclic water clusters at the CP.[25] We also found a similarity in the milder change in the degree of dissociation from the water dimer to the monomers near the CP,[40] as shown in Figure 2a.

If only two species of monomers and cyclic tetramers exist in supercritical methanol at the CP, the mole fractions are calculated to be 88.7% for the monomer and 11.3% for the cyclic tetramer using eqs 3 and 4 with the degree of dissociation of 0.662 from the cyclic tetramer to the monomers in Table 2. Even if we consider the degrees of dissociation of 0.198 from the cyclic tetramer to the dimers (not shown in Table 2) and of 0.769 from the dimer to the monomers at the CP, we obtained the mole fractions to be 88.5% for the monomer, 10.3% for the cyclic tetramer, and 1.2% for the dimers using the following equations for the mole fraction formula that are derived from the cyclic tetramer-dimer-monomer equilibrium of dissociation:

$$\text{cyclic tetramer:} \quad (1 - \alpha_{41})(1 - \alpha_{42})/M_T \tag{6}$$

$$\text{dimer:} \quad 2(1 - \alpha_{41})\alpha_{42}(1 - \alpha_{21})/M_T \tag{7}$$

$$\text{monomer:} \quad 4\{(1 - \alpha_{41})\alpha_{42}\alpha_{21} + \alpha_{41}(1 - \alpha_{42})\}/M_T \tag{8}$$

where the degrees of dissociation are $\alpha_{41} = 0.662$, $\alpha_{42} = 0.198$, and $\alpha_{21} = 0.769$ and the total mole fraction, M_T, is the sum of the numerators of eqs 6−8. We can derive eqs 6−8 when only the cyclic tetramer has an initial concentration. We have checked that the degree of dissociation from the cyclic tetramer to the trimer (chain or cyclic) plus monomer is not a serious value. Therefore, this composition obtained using eqs 6−8 does not change in the former composition using eqs 3 and 4 without the contribution of the dimer, indicating the predominant existence of the monomer and the cyclic tetramer at the CP. This result supports the recent experimental results showing the existence of the cyclic-type oligomers in supercritial methanol.[13] It seems that the monomer-tetramer (chain or cyclic) equilibrium should be the predominant equilibrium in the liquid state of methanol by the measurements.[41] The diagram of the degree of dissociation from the cyclic tetramer to the dimers for a wide range of temperature and pressure containing the CP is also drawn in Figure 2c, which shows a smaller change near the CP compared to that from cyclic tetramer to the monomers in Figure

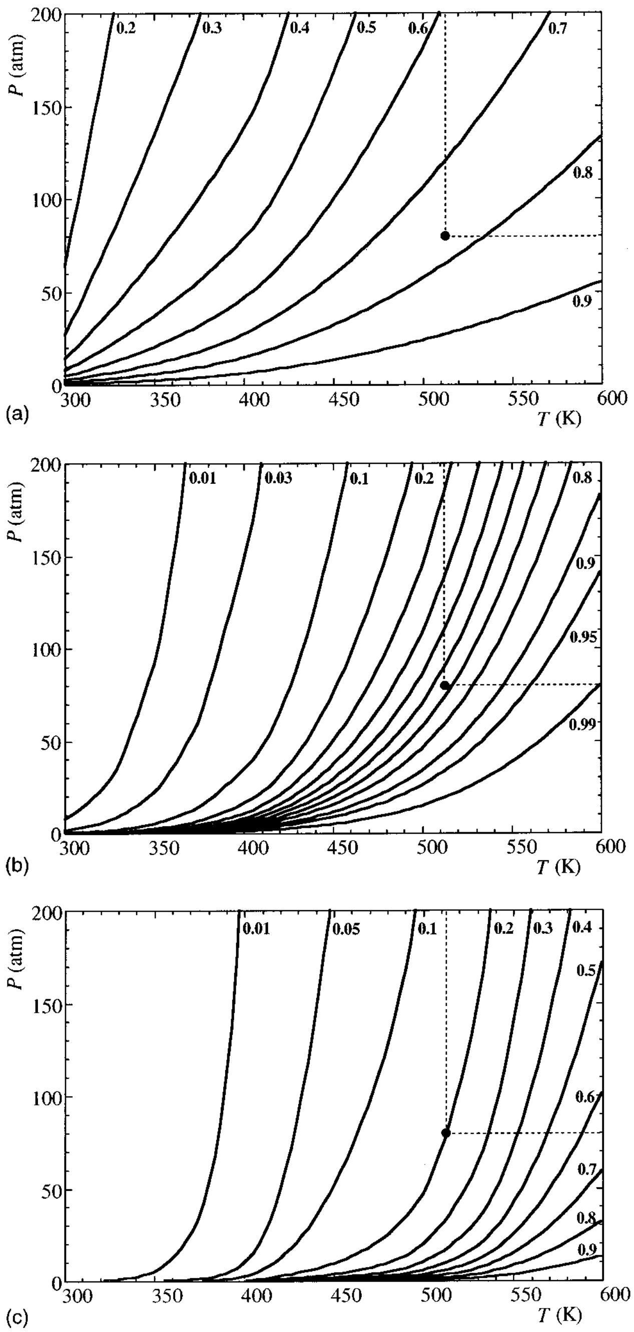

Figure 2. Degree of dissociation from the dimer to the monomers (a), from the cyclic-tetramer to the monomers (b), and from the cyclic-tetramer to the dimers (c) versus temperature and pressure. The critical point and the supercritical state are, respectively, shown the bold circle and the upper right-hand corner divided by the dotted lines.

2b. Although it has been unclear whether methanol clusters dissociate from *n*-mer to monomers directly or ($n-1$)-mer sequentially at the CP, the above results suggest that the final cluster size nearly falls into cyclic tetramers and/or monomers because both the *n* and ($n-1$)-mers, except for the cyclic tetramers, tend to dissociate into monomers. Thus, there is an insignificant contribution of the less stable isomers of each *n*-mer cluster to the mole fractions at the CP due to having a larger degree of dissociation compared to the cyclic tetramers. Therefore, we found that there should be a predominant existence of the cyclic tetramers, except for the monomer, rather than the dimers in supercritical methanol, which is in contrast to the previous calculated results[25] for supercritical water that indicate the composition of, except for 80% monomer, 20% dimer with little existence of a larger size of clusters at the CP. For methanol, we also expect in Figure 2 that the existence of the dimer should be more favorable than that of the cyclic tetramer when nearing the CP of water. In the next section, based on the assumption of the latter composition of methanol at the CP, we estimated the OH proton chemical shifts in supercritical methanol.

C. Chemical Shifts of OH Protons. The chemical shifts of the OH proton in both the monomer and clusters referenced to the averaged value of the magnetic shielding constants of methyl protons in the methanol monomer are shown in Figure 1. In Figure 1, the chemical shift of the OH proton of monomer δ_{monomer} is -3.15 ppm, which is a value similar to the -3.3 to -3.45 ppm referenced to the methyl proton in the recent NMR studies.[11,12,39] The experimental chemical shift difference between the OH proton of the monomer and of the cluster is -4.70 ppm for the tetramer,[42] which is close to the corresponding calculated values of -5.10 (-5.18) ppm for the cyclic (chain) tetramer. However, it is different from those of -3.71 (-3.92) ppm for the cyclic (chain) trimer and -5.58 (-5.37) ppm for the cyclic (chain) pentamer. We thus think that the present level of calculations can reproduce the valid chemical shifts of the OH proton of the methanol clusters. Although there is a small change in the chemical shifts of the non-hydrogen-bonded OH protons with the increasing chain cluster size ($n = 2-5$), those of the hydrogen-bonded OH proton move significantly to a higher frequency (i.e., less shielded) with an increase in both the chain and cyclic cluster size. We have also calculated the chemical shifts of the OH protons in the branched clusters, as shown in Figure 1f−h, though there is an unclear characteristic due to their irregular structures. The dependence of the chemical shifts of the hydrogen-bonded proton in the chain and cyclic clusters on the reciprocal number of the cluster size, 1/*n*, is shown in Figure 3a; these hydrogen-bonded protons correspond to the bold letters in Figure 1a−e. Figure 3b shows the decrease in the charge densities of the protons versus the reciprocal number of the cluster size 1/*n*; here the Mulliken atomic charge of the OH proton of the monomer is taken as the standard. The previous calculated results[25] for the cyclic water clusters are also shown for comparison in Figure 3a,b. For the water clusters in Figure 3a, the data were referenced to the benzene proton. The data for the chemical shifts and the decrease in the charge densities of the protons in both chain and cyclic methanol clusters, except for the cyclic methanol trimer, are well aligned on a straight line, like data for the cyclic water clusters. The difference in the decrease in charge density between methanol and water increases with the increasing size of the clusters because the methyl groups of an electron donor supply the inductive electron density to the hydrogen bonds of the methanol clusters. On the other hand, we found a similarity in the slopes of the straight line for methanol relative to that for water in Figure 3a, which may be a common characteristic of the simple clusters formed by the hydrogen-bonded OH proton and also detected in other alcohol clusters.

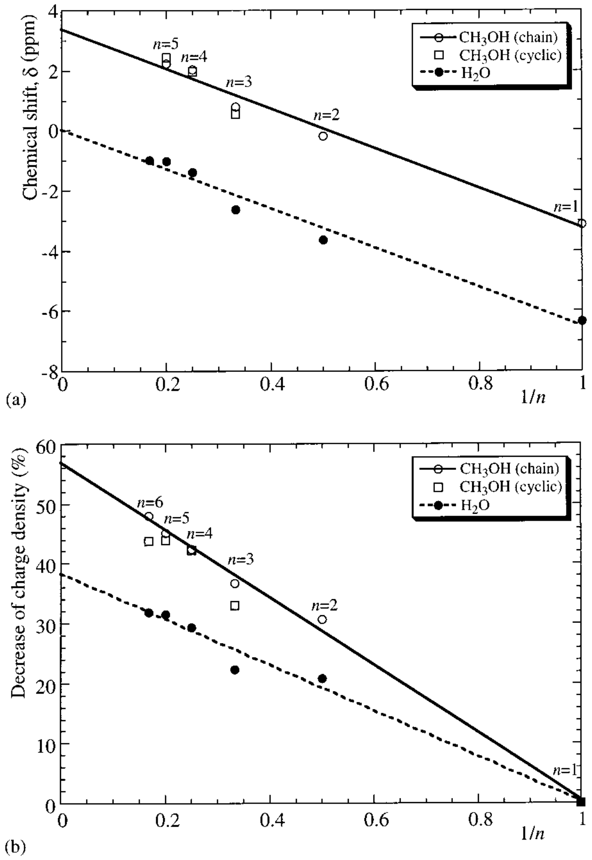

Figure 3. (a) Chemical shifts and (b) decrease of charge densities of the hydrogen-bonded proton of the chain and cyclic methanol clusters vs the reciprocal number of the cluster size 1/*n*. The protons correspond to the bold letters in Figure 1a−e. The data of water is in ref 25 for comparison.

The magnetic shielding constant in the GIAO method using atomic orbitals throughout is the sum of the diamagnetic shielding and paramagnetic shielding terms.[27] It is commonly assumed that the paramagnetic shielding term of the ^{1}H-proton contributes insignificantly to the chemical shifts due to the larger energy difference between the 1s and the other atomic orbitals, e.g., 2p with angular momentum. The diamagnetic shielding constant, σ_{dia}, of the ^{1}H-proton decreases with decreasing electron density, $\rho(r)$, namely, the partial removal of electron densities from the vicinity of the nucleus in the mean value of $1/r$ as follows:[43,44]

$$\sigma_{\text{dia}} = \frac{e^2}{3mc^2}\int \frac{\rho(r)}{r}\,\mathrm{d}v = \frac{e^2}{3mc^2}\left\langle \frac{1}{r} \right\rangle \qquad (9)$$

The linear relation between 1/*n* and both the chemical shifts and the charge densities, $\rho(r)$, of the hydrogen-bonded protons indicates that the σ_{dia} contributes mainly to the chemical shifts, namely, $\langle 1/r \rangle$ is proportional to $1/n$, in the supermolecular treatment of each cluster. The wave function of the hydrogen-bonded proton then spreads over the clusters through the hydrogen bonds, which leads to decreasing the charge density with the increasing cluster size. Because of the much smaller $O_A-H\cdots O_B$ bond angles of ~150° in the cyclic trimer than those in the other cyclic clusters, there is a smaller overlap integral between the hydrogen H and oxygen O_B compared to

TABLE 3: Calculated Chemical Shifts δ (in ppm) of Hydrogen-Bonded Proton in the Methanol Clusters Along with the Experimantal Data

	calcd	expt		
	this work[a]	ref 11	ref 12	ref 39
normal state, δ_{NS}[b]	3.38	1.55	2.26	1.5[g]
zero-density limits, $\delta_{monomer}$[c]	−3.15	−3.40	−3.45	−3.3[g]
critical point	−2.00 (−1.39)[d]	−2 to −2.2e	≈−2[f]	−

[a] Relative values to the isotropic chemical shift $[(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3]$ of the averaged value (28.43 ppm) of the methyl protons of methanol monomer. [b] $1/n = 0$ in Figure 3a. [c] $n = 1$ in Figure 3a. [d] δ_{THE} of eq 12 (δ_{EXP} of eq 11). [e] Estimated from Figure 2 in the reference. [f] Estimated from Figure 2 in the reference. [g] Estimated from Figure 1 in the reference.

the other cyclic clusters. This thus causes a small charge transfer from the H of the donor to the O_B of the acceptor, and then the chemical shifts of the hydrogen-bonded protons in the cyclic trimer move to a lower frequency (i.e., more shielded), such as that of the cyclic water trimer.[25] The calculated chemical shifts of the proton in methanol are summarized for comparison with the experimental results in Table 3. The δ_{NS} corresponds to the chemical shift of $1/n = 0$ ($n = \infty$; an infinite membered cluster) in Figure 3a. It can be seen in Table 3 that the calculated δ_{NS} is larger than the measurements; however, we think that the chemical shifts of the hydrogen-bonded proton in Figure 3a will saturate at about <3.0 ppm because of the tendency toward a smaller change in the chemical shifts in larger size ($n = 4-5$) clusters. The following total chemical shift, δ_{EXP}, is often used to explain the experimental data[12,45,46]

$$\delta_{EXP} = m_{HB}\delta_{HB} + m_{NHB}\delta_{NHB} = m_{HB}\delta_{NS} + m_{NHB}\delta_{monomer} \tag{10}$$

where m_{HB} and m_{NHB} ($= 1 - m_{HB}$) are, respectively, the mole fractions of the hydrogen-bonded proton and the non-hydrogen-bonded proton and δ_{HB} and δ_{NHB} correspond, respectively, to δ_{NS} and $\delta_{monomer}$ in Table 3. Equation 10 is then rewritten as eq 11 using the composition ($x_{monomer} = 0.885$; $x_{dimer} = 0.012$; $x_{cyclic-tetramer} = 0.103$) of the supercritical methanol at the CP

$$\delta_{EXP} = (x_{dimer}/2 + 4{\cdot}x_{cyclic-tetramer})\delta_{NS} + \{(x_{dimer}/2) + x_{monomer}\}\delta_{monomer} \tag{11}$$

Because δ_{EXP} does not describe the difference in the proton chemical shifts of the different clusters, we can then suggest the following equation instead of δ_{EXP}:

$$\delta_{THE} = \{(x_{dimer}/2)\delta_{dimer,HB} + 4x_{cyclic-tetramer}\delta_{cyclic-tetramer}\} + \{(x_{dimer}/2)\delta_{dimer,NHB} + x_{monomer}\delta_{monomer}\} \tag{12}$$

where $\delta_{dimer,HB}$ (−0.20 ppm), $\delta_{dimer,NHB}$ (−3.00 ppm), and $\delta_{cyclic-tetramer}$ (+1.95 ppm) are, respectively, the chemical shifts of the hydrogen-bonded and the non-hydrogen-bonded OH protons in the dimer (see Figure 1b) and the chemical shifts of the hydrogen-bonded OH protons in the cyclic tetramer (see dashed stick in Figure 1d). If we know the mole fractions of clusters at a range of temperature and pressure, we can theoretically estimate the chemical shifts of the OH proton in methanol by extending eq 12 to larger size clusters. The calculated results of the total chemical shifts of the hydrogen-bonded proton at the CP using eqs 11 and 12 are listed in Table 3. We find that the δ_{THE} is excellent consistent with the experimental data compared to the δ_{EXP}. Although we cannot make a simple comparison between the experimental and calculated chemical shifts at the CP because the former shows a slight broad uncertainty caused by thermal fluctuation with the phase transition, we think that the consistence of the δ_{THE} with the measurements indicates that the gas-phase approximation using the cluster model can describe sufficiently the NMR chemical shift of the hydrogen-bonded proton in supercritical methanol.

IV. Conclusions

We have theoretically estimated the chemical shifts of the OH proton in supercritical methanol using the ab initio MO method at the MP2 level of theory. The degree of dissociation from the hydrogen-bonded clusters to the monomers indicated that supercritical methanol is comprised of 89% monomer and 10% cyclic tetramer plus only a few dimers of ∼1% at the CP. The predominant existence of the cyclic tetramers rather than the dimers in supercritical methanol is in contrast to previous theoretical results for supercritical water that indicate the composition of, except for 80% monomer, 20% dimer with little existence of a larger size of clusters at the CP. We also found that a significant fluctuation of the composition of methanol should be caused by a greater change in the degree of dissociation of the cyclic tetramer compared to the dimer near the CP. We have determined the proton NMR chemical shift to be −2.00 ppm based on the assumption of the composition of methanol at the CP, which excellently reproduces the recent NMR data of −2.0 to −2.2 ppm in supercritical methanol. We suggest that the gas-phase approximation using the cluster model can well describe the NMR chemical shift of the hydrogen-bonded proton in supercritical methanol, such as in the previous theoretical study of supercritical water.

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