

Dipolar Hydration Anomaly in the Temperature Dependence: Carbonyl and Nitrile Solutes Studied by ^{13}C NMR Chemical Shifts

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The ^{13}C chemical shifts δ of carbonyl ($^{13}\text{C}=\text{O}$) and nitrile ($^{13}\text{C}\equiv\text{N}$) compounds in aqueous solutions were measured as functions of temperature to study the hydration structure around dipolar solutes. The δ values showed an anomalous maximum in the temperature dependence; at $-9\text{ }^\circ\text{C}$ for urea, at $23\text{ }^\circ\text{C}$ for diethyl ketone, at $24\text{ }^\circ\text{C}$ for cyanamide, at $32\text{ }^\circ\text{C}$ for acetone, at $63\text{ }^\circ\text{C}$ for acetaldehyde, and at $96\text{ }^\circ\text{C}$ for acetonitrile. No such anomaly was observed in any other organic solvents. The presence of the maximum is due to the competition of two factors, solute–solvent and solvent–solvent interactions. One is the electrostatic hydrogen bond between the solute and water, and the other is the hydrogen bond network characteristic of solvent water. When the network structure of water is collectively stabilized with decreasing temperature, the effective water–water interaction becomes stronger than the solute–water interaction, giving the maximum in the temperature dependence of δ . The temperature of the maximum chemical shift $T_{\max\delta}$ was found to be sensitive to the solute polarity. The solute dependence of $T_{\max\delta}$ was explained in terms of the solute dipole moment μ obtained from ab initio calculations: the larger the μ , the lower the $T_{\max\delta}$.

1. Introduction

Water forms a variety of hydration structures in aqueous solutions as a result of the competition between solute–water interaction and hydrogen bond (HB) network formation characteristic of solvent water.^{1–4} The hydration structures play an important role in many chemical and biological processes; e.g., solubilities, mobilities, and associations are quite different among ionic, dipolar, and nonpolar solutes, which perturb the water structure in different ways. For a better and general understanding of the hydration phenomena, it is necessary to elucidate these hydration structures in terms of the competition of the molecular interactions involved.

Among the variety of hydrations, as illustrated in Figure 1, ionic hydration is one extreme of the strong solute–water interaction, while nonpolar or hydrophobic hydration is the other extreme of the weak solute–water interaction. In this study, we focus on dipolar hydration, which is an intermediate between these extremes; systematic research on such intermediate hydrations is quite rare^{5–8} in comparison with that on ionic and hydrophobic hydrations.^{9,10} Here we aim to clarify how the dipole–water interaction competes with the surrounding water–water HBs, depending on the temperature and the solute polarity. We investigate the competition by variable-temperature ^{13}C NMR spectroscopy.

To probe the hydration structure around dipolar solutes, we need to directly monitor the solute–water interaction from the solute side. This is in contrast to the traditional approaches, where hydrations are usually characterized from the solvent side

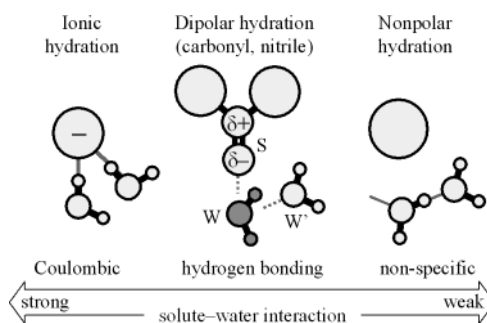


Figure 1. Solute–water interactions and their corresponding hydration structures. In the dipolar hydration structure, the electrostatic hydrogen-bonding interaction between the solute S and its neighboring water W is in a comparable competition with the hydrogen bond formation between the solvent waters W and W'.

only. It has been often questioned whether the HB structure of water is distorted or developed by solutes, some being called structure-breakers and others structure-makers.^{1–4} Such a solvent-sided view, however, is inadequate for the dipolar hydration study. This is mainly because the perturbation of water properties by dipolar solutes is much smaller than those by ionic and hydrophobic solutes.^{11–14} Dipolar solutes (alcohols, amines, carbonyls, and nitriles) can form an HB with solvent water, and the dipole–water HB is energetically comparable with the water–water HB. Thus, the solute–water HB formation instead of the water–water one has a small effect on the interaction exerted on the water molecule, whereas it considerably affects the interaction on the dipolar solute. Another reason is that most of the dipolar solutes are amphiphilic, containing a hydrophobic residue. Thus, the solvent water structure is inevitably perturbed by the hydrophobic moiety as well as by the dipolar part.^{15–17}

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To separate the dipolar hydration effect from the hydrophobic one, it is indispensable to monitor the solute–water HB itself from the solute side. In the present work, we choose carbonyl and nitrile compounds as dipolar solutes and measure their ^{13}C chemical shifts, $\delta(^{13}\text{C}=\text{O})$ and $\delta(^{13}\text{C}\equiv\text{N})$, which are sensitive enough to the solute–water HB interaction.¹⁸

The dipolar hydration structure can be sensitive to the temperature and the solute polarity. This is by virtue of the subtle balance between the two competing HB interactions: one is the HB structure of water, which develops with decreasing temperature T , while the other is the solute–water HB, which is more stabilized with increasing solute dipole moment μ . At higher T and larger μ , the water W in Figure 1 will be preferentially oriented to the solute S by breaking the water–water HB, as in the ionic hydration. On the other hand, at lower T and smaller μ , the water W will form a stronger HB with the neighboring water W' by minimizing the solute–water interaction, as in the hydrophobic hydration. We can thus expect a wide range of hydration structures as a function of T and μ . Here we have examined the temperature dependence of the ^{13}C chemical shifts δ , and found an anomalous maximum indicating the above-mentioned competition between the solute–solvent and solvent–solvent interactions. We further compare various solutes with respect to the temperature of the maximum chemical shift $T_{\max \delta}$, where we show a clear correlation that the larger the μ , the lower the $T_{\max \delta}$.

The experimental procedure is shown in section 2. In section 3, we present the anomalous maximum found in the temperature dependence of δ . In section 4, the solvent and concentration effects are discussed to prove that the HB network of water plays a key role in the anomaly. In section 5, we compare the $T_{\max \delta}$ values of various solutes. In section 6, the solute dependence of $T_{\max \delta}$ is explained in terms of the solute polarity. Conclusions are given in section 7.

2. Experimental Section

Acetaldehyde (99.5%, Aldrich), acetone (99.5%, Wako), methyl ethyl ketone (99.5%, Kanto), diethyl ketone (99%, Kanto), urea (99%, Aldrich), acetonitrile (99.5%, Kanto), and cyanamide (99%, Aldrich) were used as received. Aqueous solutions of the carbonyl and nitrile compounds were prepared at a concentration of 0.010 mol/dm³. Water (H_2O) was purified to the specific resistance of 18 M Ω ·cm by an Organo Puric-Z. Methanol (99.8%, Wako) was used after being dried by molecular sieves 3A (Nacalai). Deuterium oxide (99.8%, Merck), dimethyl sulfoxide (99%, Kanto), ethylene glycol (99.5%, Kanto), formic acid (98%, Kanto), tetrachloromethane (99.5%, Wako), trifluoroacetic acid (99%, Kanto), and 2,2,2-trifluoroethanol (98%, Kanto) were used without purification.

The ^{13}C and ^1H spectra were measured by a multipurpose NMR spectrometer (JEOL LA-400 wide-bore type). The temperature of the sample solution was controlled by flowing thermostated air or nitrogen gas, and was stable within ± 0.1 °C. The spatial inhomogeneity of the temperature in the sample tube was within ± 0.2 °C at 0 °C, and within ± 0.6 °C at 100 °C. The temperature T shown in this paper denotes the average temperature in the sample. The measurement of the chemical shift δ in the dilute aqueous solution was carried out with an external reference: i.e., an external magnetic field outside of the sample was used as a reference. The external magnetic field produced by our superconducting magnet (Oxford, 9.39 T) was stable enough for this use (within 0.003 ppm in a set of measurements). The chemical shift values δ_{obsd}

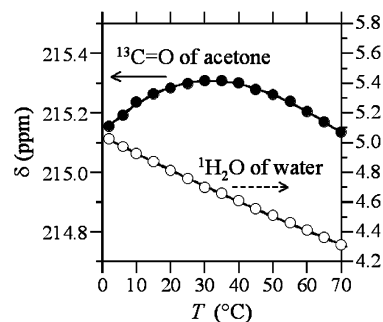


Figure 2. $^{13}\text{C}=\text{O}$ chemical shift δ of solute acetone and the ^1H chemical shift of solvent water in aqueous acetone solution as functions of temperature. The lines are polynomial fits to the data.

observed at different temperatures are influenced by the change in the *volumetric* magnetic susceptibility $\Delta\chi_v$ of the solvent water due to the Lorentz field produced in the sample solution.¹⁸ For a sufficiently long sample parallel to the external magnetic field, the susceptibility effect was corrected as follows:

$$\begin{aligned}\delta &= \delta_{\text{obsd}} - \frac{4\pi}{3}\Delta\chi_v \\ &= \delta_{\text{obsd}} - \frac{4\pi}{3}\chi_m\Delta\rho\end{aligned}\quad (1)$$

Here we assume that the *mass* magnetic susceptibility χ_m of the solvent water is independent of the temperature (-0.72×10^{-6} cm³/g).¹⁹ $\Delta\rho = \rho^{\text{sample}} - \rho^{\text{reference}}$ denotes the change in the mass density of the solvent water between the sample and reference temperatures. When the reference temperature is fixed at 30 °C, the second term in eq 1 is in the range of +0.013 (4 °C) to −0.112 (100 °C) ppm.

3. Anomalous Temperature Dependence

The competition of the solute–water and water–water HBs is studied from the temperature dependences of the ^{13}C chemical shift of solute carbonyl $\delta(^{13}\text{C}=\text{O})$ and the ^1H chemical shift of solvent water $\delta(^1\text{H}_2\text{O})$. Here we choose acetone as a typical carbonyl solute. As shown in Figure 2, the $\delta(^{13}\text{C}=\text{O})$ of acetone has an anomalous maximum in the temperature dependence. The temperature of the maximum chemical shift $T_{\max \delta}$ is determined to be 32 ± 1 °C. At temperatures higher than $T_{\max \delta}$, the solute–water HB is enhanced with decreasing temperature in a way similar to that of the water–water HB; see the temperature dependences of $\delta(^{13}\text{C}=\text{O})$ and $\delta(^1\text{H}_2\text{O})$. At the lower temperatures, the solute–water HB is anomalously reduced with decreasing temperature in contrast to the monotonic increase in the water–water HB. The opposite temperature dependences of the solute–water and water–water HBs indicate the competition of these HBs in the cooled aqueous solution. In other words, the solute–water HB is made less stable by the enhanced water–water HBs, probably due to the HB network formation among the surrounding waters at the low temperatures. The role of the HB network of water in this anomaly is examined in the next section from the solvent and concentration effects on the temperature dependence of δ .

By utilizing the temperature dependence of $\delta(^{13}\text{C}=\text{O})$, we further search into how the energetic stability of the solute–water HB between an acetone (A) and a specific water (W) is affected by other solvent waters. Let us assume that the average number N_{HB} of the HBs between the acetone and solvent waters

TABLE 1: Enthalpy Change ΔH_{HB} upon Hydrogen Bond Formation in a Specific Acetone–Water Pair in Aqueous Solution as a Function of Temperature T

T (°C)	ΔH_{HB} (kcal/mol)
4	$+0.078 \pm 0.004$
30	$+0.005 \pm 0.002$
60	-0.077 ± 0.004

is proportional to the chemical shift change $\Delta\delta$ induced by the solvent waters:

$$N_{\text{HB}} \propto \Delta\delta = \delta - \delta_0 \quad (2)$$

where δ_0 denotes the $^{13}\text{C}=\text{O}$ chemical shift of an isolated acetone molecule (196.7 ppm).²⁰ N_{HB} is expressed in terms of the molarity equilibrium constant K_{AW} for HB formation in the A–W pair ($\text{A} + \text{W} \rightleftharpoons \text{AW}$) as²¹

$$N_{\text{HB}} = K_{\text{AW}}[\text{H}_2\text{O}] \quad (3)$$

where $[\text{H}_2\text{O}]$ is the molarity of the solvent water. The equilibrium constant K_{AW} is related to the Gibbs free energy change ΔG_{HB} upon HB formation in the A–W pair:²²

$$K_{\text{AW}}[\text{H}_2\text{O}] = \exp(-\Delta G_{\text{HB}}/k_{\text{B}}T) \quad (4)$$

where k_{B} is the Boltzmann constant. According to eqs 2–4, the temperature dependence of $\Delta\delta$ at a constant pressure P is controlled by ΔG_{HB} as

$$\Delta\delta \propto \exp(-\Delta G_{\text{HB}}/k_{\text{B}}T) \quad (5)$$

From the van't Hoff analysis of eq 5, the corresponding enthalpy change ΔH_{HB} can be obtained by

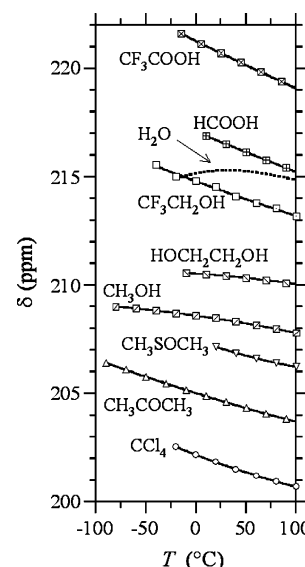
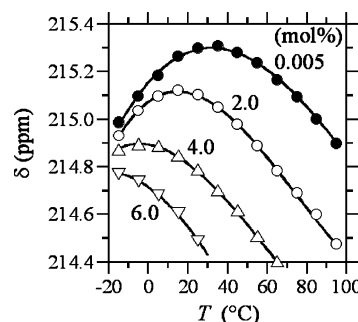
$$\Delta H_{\text{HB}} = k_{\text{B}}T^2 \left[\frac{\partial \ln(\Delta\delta)}{\partial T} \right]_P \quad (6)$$

The ΔH_{HB} values calculated at various temperatures are listed in Table 1. At a high temperature (60 °C), ΔH_{HB} is a small negative: i.e., the acetone–water HB formation is slightly exothermic. With decreasing temperature, however, ΔH_{HB} shows a monotonic increase with a negative heat capacity change, $\Delta C_P = (\partial \Delta H_{\text{HB}} / \partial T)_P = -2.8 \text{ cal/mol}\cdot\text{K}$, and changes to a small positive at temperatures lower than $T_{\text{max}} \delta$. Thus, the acetone–water HB formation is destabilized by the solvent water from the exothermic to the endothermic conditions with decreasing temperature passing through $T_{\text{max}} \delta$.

The temperature-sensitive control of the solute–water interaction is by virtue of the subtle balance between the solute–water HB and the effective water–water interaction. In the absence of solvent water (i.e., in the gas phase), the HB formation energy in an acetone–water dimer $\Delta E_{\text{HB}}^{\text{vac}}$ is estimated to be ca. -4.3 kcal/mol by an ab initio calculation.²³ The binary interaction energy is a large negative, whereas the ΔH_{HB} observed in the aqueous solution is almost zero. This means that the binary attractive interaction in the acetone–water pair is nearly canceled by the indirect interaction through the solvent waters, i.e., the hydration effect on the solute–water pair.

4. Solvent and Concentration Effects

The solvent and concentration effects on $\delta(^{13}\text{C}=\text{O})$ are investigated here to verify that the HB network of solvent water plays a key role in the competition of the solute–water and water–water HBs.

**Figure 3.** Solvent effect on the temperature dependence of the $^{13}\text{C}=\text{O}$ chemical shift δ of acetone.**Figure 4.** Concentration effect on the temperature dependence of the $^{13}\text{C}=\text{O}$ chemical shift δ of acetone in aqueous solutions at various mole fractions of acetone.

First, we compare the temperature dependences of δ in various organic solvents, aprotic solvents (CCl_4 , CH_3COCH_3 , and CH_3SOCH_3) and protic ones though less structured than water (CH_3OH , $\text{HOCH}_2\text{CH}_2\text{OH}$, $\text{CF}_3\text{CH}_2\text{OH}$, HCOOH , and CF_3COOH), as summarized in Figure 3. The δ values are in the range of 200–222 ppm, and the larger δ indicates the larger proton-donating ability of the solvent.¹⁸ In the temperature dependences of δ , however, no anomalous maximum is observed in any solvents other than water. The comparison tells us that the maximum presence arises from the HB structure characteristic of solvent water.²⁴

Second, we examine the concentration effect on δ in binary mixtures of acetone and water.²⁵ The HB structure of water in the mixture can be controlled by varying the concentration of acetone. With increasing acetone mole fraction, the HB network of water is more disrupted by the acetone molecules. Figure 4 shows the concentration effect on the temperature dependence of δ including the supercooled conditions down to -15°C . In the dilute aqueous acetone solution (0.005 mol %), the maximum is observed at $32 \pm 1^\circ\text{C}$. With increasing acetone mole fraction, the maximum evidently shifts to lower temperatures; $T_{\text{max}} \delta = 14 \pm 2^\circ\text{C}$ at 2.0 mol %, and $-3 \pm 2^\circ\text{C}$ at 4.0 mol %. At acetone mole fractions higher than 6.0 mol %, no maximum is observed in the temperature range covered. The shift of $T_{\text{max}} \delta$ to lower temperatures indicates that the acetone–water HB formation is less disturbed by the surrounding water–water HBs with decreasing water mole fraction. The concentration effect

TABLE 2: Properties of the Carbonyl and Nitrile Compounds Studied^a

compound			$T_{\max \delta}$ (°C)	q_C (e)	q_O or q_N (e)	δq (e)	l (Å)	μ (D)
acetaldehyde	CH ₃ -CO-H	○	63 ± 1	+0.260	-0.372	0.316	1.182	1.79
acetone	CH ₃ -CO-CH ₃	⊙	32 ± 1	+0.272	-0.397	0.335	1.187	1.91
methyl ethyl ketone	CH ₃ -CO-C ₂ H ₅	⊖	35 ± 1	+0.293	-0.405	0.349	1.187	1.99
diethyl ketone	C ₂ H ₅ -CO-C ₂ H ₅	⊕	23 ± 2	+0.322	-0.413	0.368	1.188	2.10
urea	NH ₂ -CO-NH ₂	▽	-9 ± 2	+0.624	-0.497	0.561	1.192	3.21
acetonitrile	CH ₃ -CN	●	96 ± 2	+0.067	-0.340	0.204	1.129	1.11
cyanamide	NH ₂ -CN	▼	24 ± 2	+0.358	-0.374	0.367	1.131	1.99

^a $T_{\max \delta}$ = temperature of the maximum $^{13}\text{C}=\text{O}$ or $^{13}\text{C}\equiv\text{N}$ chemical shift in the aqueous solution; q_C , q_O , and q_N = partial atomic charges on the carbon, oxygen, and nitrogen atoms, respectively, calculated in the gas phase; δq = magnitude of the dipolar charges on the carbonyl or nitrile group defined in eqs 8 and 9; l = length of the C=O or C≡N bond; μ = dipole moment of the carbonyl or nitrile group defined in eq 7.

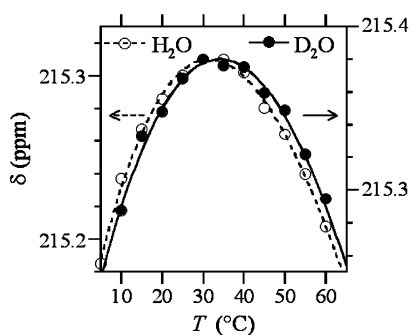


Figure 5. Solvent isotope effect between H₂O and D₂O on the temperature dependence of the $^{13}\text{C}=\text{O}$ chemical shift δ of acetone.

also suggests the importance of the collective HB property of water in the HB competition.

Third, we inspect the solvent isotope effect on δ by replacing the solvent water from H₂O to D₂O. It is well-known that the deuteration has a substantial effect on the physical properties of water;²⁶ e.g., the temperature of the maximum water density $T_{\max \rho}$ increases from 4 to 11 °C. This is because the deuteration strengthens the HB interaction between the water molecules.^{27–29} In the dipolar hydration studied here, the enhanced water–water HB will disturb the competing solute–water HB formation more. Accordingly, the solvent deuteration is expected to increase the $T_{\max \delta}$ value. In Figure 5, to be sure, the $T_{\max \delta}$ value increases from 32 ± 1 (H₂O) to 34 ± 1 (D₂O) °C, but the change in $T_{\max \delta}$ is much smaller than that in $T_{\max \rho}$. The small isotope effect on $T_{\max \delta}$ is accounted for by the cancellation of the two competing enhancements: i.e., the solvent deuteration enhances not only the water–water HB but also the solute–water HB; see the maximum δ value in D₂O (215.38 ppm) larger than that in H₂O (215.31 ppm). The weak isotope effect on $T_{\max \delta}$ is in favor of our picture of the dipolar hydration structure based on the competition of the HB interactions.

5. Solute Dependence

To shed light on the solute dependence of the dipolar hydration structure, we compare the ^{13}C chemical shifts δ of various carbonyl and nitrile solutes listed in Table 2. The solute molecules studied here are composed of a polar part (carbonyl or nitrile group) and its residual moieties (alkyl chains with various lengths or amino groups). By systematically substituting the residual moieties, we can control the dipole moment of the polar part and the relative contribution of the hydrophobicity.

The temperature dependences of δ for these solutes are summarized in Figure 6. A maximum is actually observed for every solute. The presence of the maximum indicates that the competition of the solute–water and water–water HBs is a feature common to the dipolar hydration. It is to be noted that

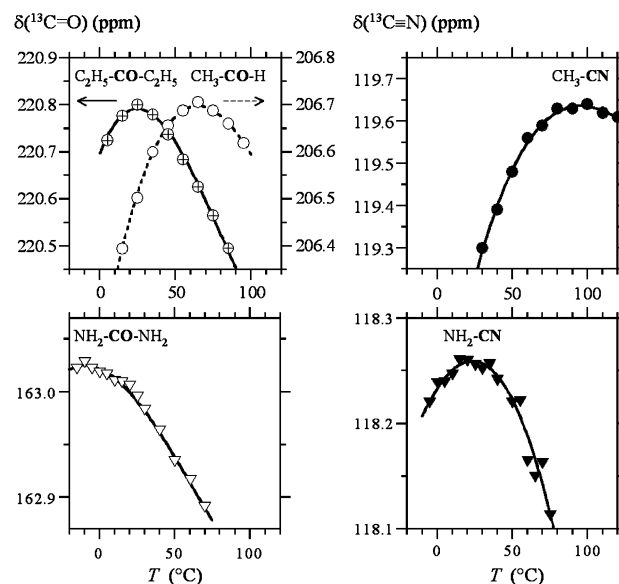


Figure 6. Temperature dependence of the $^{13}\text{C}=\text{O}$ and $^{13}\text{C}\equiv\text{N}$ chemical shifts δ for various carbonyl and nitrile solutes in the aqueous solutions.

the temperature of the maximum chemical shift $T_{\max \delta}$ is highly dependent on the solute molecule. As listed in Table 2, the $T_{\max \delta}$ value ranges widely from -9 °C for urea to +96 °C for acetonitrile. Here we can easily see that the $T_{\max \delta}$ values of the amino-substituted solutes (urea and cyanamide) are lower than those of the corresponding methyl-containing solutes (acetone and acetonitrile, respectively). In addition, the $T_{\max \delta}$ values of the carbonyl solutes (acetone and urea) are lower than those of the corresponding nitrile solutes (acetonitrile and cyanamide, respectively).

Before explaining below the solute dependence of $T_{\max \delta}$ in terms of the solute dipole moment, we show that the hydrophobic hydration effect of the residual group is negligible compared with the overwhelming dipolar hydration effect. The hydrophobicity of the alkyl group is known to enhance the HB structure among the surrounding waters, commonly referred to as the structure-making effect.^{1–4} If the hydrophobic hydration effect is important in the competition of the HBs, the longer alkyl chains will disturb the solute–water HB formation more, giving higher $T_{\max \delta}$ values. This is not the case, however, as shown in Figure 6. The $T_{\max \delta}$ value rather decreases with increasing alkyl chain length, 63 ± 1 °C for acetaldehyde to 23 ± 1 °C for diethyl ketone. In fact, the anomalous maximum does appear for entirely hydrophilic solutes, such as urea and cyanamide, without any alkyl chain. As a result, the hydrophobicity of the residual moiety is irrelevant to the maximum presence. In this respect, the anomaly found here in the dipolar hydration is completely different from the known anomalies in the amphiphilic hydration; the amphiphilic hydration anomalies

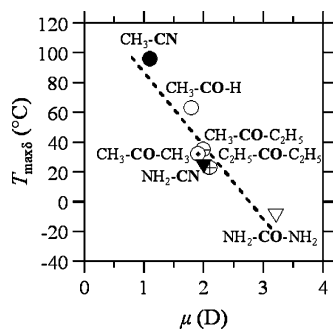


Figure 7. Correlation between the $T_{\max \delta}$ and μ values of the carbonyl and nitrile compounds. The dotted line is the linear fit to the data.

are caused by the hydrophobic hydration effect, and are often observed in the solute concentration dependence of the water properties, such as the ^1H chemical shift of the solvent water.³⁰

6. Correlation with Solute Dipole Moment

Now we explain the solute dependence of $T_{\max \delta}$ by using an index characterizing the solute polarity. As such a polarity index, we introduce the partial dipole moment μ of the carbonyl and nitrile groups of the solute molecules:

$$\mu = (\delta q)l \quad (7)$$

where δq is the magnitude of the dipolar charges located on the carbonyl or nitrile group and l is the distance between the dipolar charges. Here we define δq as follows:

$$\delta q = (q_{\text{C}} - q_{\text{O}})/2 \quad \text{for carbonyl molecules} \quad (8)$$

$$\delta q = (q_{\text{C}} - q_{\text{N}})/2 \quad \text{for nitrile molecules} \quad (9)$$

where q_{C} (>0), q_{O} (<0), and q_{N} (<0) denote the partial charges on the carbon, oxygen, and nitrogen atoms, respectively. The partial charges were calculated by the GAUSSIAN 98 program³¹ at the Hartree–Fock level of approximation with the 6-311G** basis set and the Mulliken population analysis in the gas phase.³² We also determined the distance l between the charges (i.e., the length of the $\text{C}=\text{O}$ or $\text{C}\equiv\text{N}$ bond) from the ab initio calculations. The charges, distances, and partial dipole moments thus calculated are listed in Table 2. The δq value changes widely from 0.204e (electrons) for acetonitrile to 0.561e for urea. In contrast, the variation in l is less than 0.07 Å. Thus, the solute dependence of μ is dominated by the variation in δq . The variation in δq is explained in terms of the electron-donating ability of the residual group; the δq value becomes larger with increasing alkyl chain length and upon substitution of the alkyl group to the amino one. It is also to be noted that the carbonyl compounds have larger μ values than those of the corresponding nitrile compounds. In Figure 7, we plot $T_{\max \delta}$ against μ . A clear correlation is found that the larger the μ , the lower the $T_{\max \delta}$. This manifests the competition of the solute–water and water–water HBs. When the electrostatic solute–water HB is stabilized by the larger μ , the competing contribution of the HB network of solvent water is suppressed to a considerable extent, resulting in the decrease in $T_{\max \delta}$. Summarizing the above information, the competition of the solute–water and water–water HBs in the dipolar hydration structure is systematically controlled by the solute dipole moment and the temperature.

Such a temperature-sensitive competition in hydration structure can be observed not only in the dipolar hydration but also in the ionic one. An analogy we notice is the temperature-induced change from the negative hydration to the positive

one.^{33–35} At low temperatures, such larger monatomic ions as Na^+ and Cs^+ are known to accelerate the rotational motion of the hydrating waters by breaking the water–water HBs in their hydration shell, referred to as the negative hydration. In contrast, at high temperatures where the water–water HBs are weakened, the rotational motion of the hydrating waters is rather hindered by the ion–water Coulombic attraction, the so-called positive hydration. In this case, the competition takes place between the ion–water and water–water interactions, and is controlled by the temperature and the surface charge density of the ionic solutes.

In subsequent works, we will extend the temperature range from ambient to lower and higher, to explore a wide variety of hydration structures.³⁶ At the lower temperatures in the clathrate hydrate regime, the water–water HB is more stabilized to form a rigid cage structure around the guest molecule. At the higher temperatures in the sub and supercritical states, the HB network of water is completely disrupted. The dipolar hydration studies under these extreme conditions will provide more general pictures of the hydration structures and the molecular interactions involved.

7. Conclusions

The competition of the solute–water and water–water HBs in a dipolar hydration structure was studied from the temperature dependence of the $^{13}\text{C}=\text{O}$ and $^{13}\text{C}\equiv\text{N}$ chemical shifts δ of the carbonyl and nitrile solutes. We found an anomalous maximum in the temperature dependence of δ . The maximum indicates that the solute–water HB competes with the surrounding water–water HBs, which develop at lower temperatures. The solvent and concentration effects on the maximum made it clear that the HB network of solvent water plays an important role in the competition of the HBs. The temperature of the maximum chemical shift $T_{\max \delta}$ measured for various solutes ranged widely from $-9\text{ }^{\circ}\text{C}$ for urea to $+96\text{ }^{\circ}\text{C}$ for acetonitrile. The solute dependence of $T_{\max \delta}$ was explained in terms of the dipole moment μ of the solute molecule: the larger the μ , the lower the $T_{\max \delta}$. The correlation proves that the competition of the solute–water and water–water HBs is controlled by the solute polarity and the temperature.

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- (20) To determine the ¹³C=O chemical shift δ of an isolated acetone molecule, we measured the δ value of acetone vapor confined in a quartz tube as a function of temperature from 200 to 400 °C. The ¹³C=O signal was observed at 196.7 ppm with negligible temperature dependence (<0.05 ppm). Thus, we defined this value as the δ of an isolated acetone.
- (21) From the definition of the molarity equilibrium constant $K_{AW} = [AW]/([A][W])$, the average number N_{AW} of HBs which the acetone A forms with the specific water W is given by $N_{AW} = [AW]/[A] = K_{AW}[W]$. Considering the equilibrium for each solvent water molecule, the total number N_{HB} of HBs between the acetone and (any) solvent water is expressed as in eq 3.
- (22) The Gibbs free energy change ΔG_{HB} upon HB formation in the A–W pair ($A + W \rightleftharpoons AW$) is related to the mole fractions x of the species A, W, and AW as $\exp(-\Delta G_{HB}/k_B T) = x_{AW}/(x_A x_W)$. The right side can be transformed as $x_{AW}/(x_A x_W) = ([AW]/([A][W]))(n_{total}/V)$, where n_{total} is the total number of molecules involved in the aqueous solution and V is the volume of the solution. For the dilute aqueous solution, n_{total}/V is approximately equal to the molarity of water [H₂O]. Thus, the combination of the equations above gives eq 4.
- (23) From ab initio calculations with the 6-31G** basis, the HB formation energy in an acetone–water dimer is estimated to be -4.3 kcal/mol (Zhang, X. K.; Lewars, E. G.; March, R. E.; Parnis, J. M. *J. Phys. Chem.* **1993**, *97*, 4320), while that in a water dimer is -5.7 kcal/mol. Thus, the binary HB interaction in an acetone–water pair is comparable with, but slightly weaker than, that in a water–water pair.
- (24) In Figure 3, to be accurate, the temperature dependence of the chemical shift δ in methanol and ethylene glycol has a slightly negative curvature ($[\partial^2 \delta / \partial T^2] < 0$), in contrast to the linear temperature dependence in other organic solvents. The negative curvature suggests a weakly ordered HB network in methanol and ethylene glycol.
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