Determination of the Hydrate Structure of an Isolated Alcoholic OH in Hydrophobic Medium by Infrared and Near-Infrared Spectroscopy

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This paper reports the structure of the hydrate complex of an isolated alcoholic OH, produced in a small amount in hydrophobic solution in heptane. The structure was determined from the changes, caused by hydration, in the infrared and near-infrared spectra of 2-nonanol in the solution. The changes were exhibited in the "difference" spectrum, in which the spectrum of the solution before hydration was subtracted from that after hydration. The difference spectrum showed a "plus" or "minus" peak at the frequency of the stretching band of a free OH, depending on whether the concentration was below or above about 2%(v/v), respectively. The *plus* peak appears because the OH stretching band of the isolated OH that acts as an *acceptor* does not change in frequency but significantly increases in intensity, in agreement with theoretical calculations. In contrast, the stretching band of an isolated OH that acts as a *donor* shifts downward. This shift decreases the intensity at the stretching frequency of a free OH, giving rise to a *minus* peak at the frequency in the *difference* spectrum. It was concluded that an isolated OH is hydrated in the manner as HO···HOH and OH···OH_2 at a concentration below and above about 2%, respectively, in the hydrophobic solution of 2-nonanol.

Introduction

Water interacts with various kinds of organic molecules through hydrogen bonding,[1] the manner and strength of which depend on the nature of the partner functional group.[1,2] Characterization of the interactions is important to understand the basic action of water in chemistry or in life. It is easier to study the interaction with a functional group that only acts as a proton acceptor to water, such as an ether O or ketone C═O.[2−5] In contrast, the interaction with an amphoteric functional group is more complicated, not only because the group can act as either a proton acceptor or a proton donor to water, but also because it forms an associated group by itself.[6]

When hydrated, an alcoholic OH group can play the role of acceptor or donor. Elucidation of the one-to-one interaction of an isolated OH with water is important as the first step in understanding complicated interactions of water with associated OH groups that commonly occur in liquids or solids. One-to-one interactions of an isolated alcoholic OH group with water have been experimentally and theoretically studied by many authors.[7−16] Experimental studies have mostly examined the complex of methanol with water.[7−9,11] Huisken and Stemmler studied the structure of a methanol−water dimer by molecular beam depletion spectroscopy and reported that methanol occupies the proton-acceptor position in the dimer.[7] Bakkas et al. studied infrared absorptions of the complex of methanol and water isolated in nitrogen[8] and argon[9] matrixes. They reported that an OH of methanol acts as a donor to water in the nitrogen matrix, and that the hydrogen-bonding energy was not much different between the two structures, in which an OH acts as a donor or an acceptor, in theoretical calculations.[8] On the other hand, they reported that the OH of methanol acts as an acceptor to water in the argon matrix.[9] Stockman et al.[11] studied a water−methanol dimer in the gaseous state by microwave rotation-tunneling spectroscopy and reported that a stable structure in supersonically cooled molecular beams corresponds to a water-donor, methanol-acceptor complex. Iwamoto et al. studied the hydrate structure of an isolated OH in poly(ethylene-co-vinyl alcohol) (EVOH), which consists of a hydrophobic CH_2CH_2 part and a hydrophilic CH_2CHOH part, of various compositions, using near-infrared spectroscopy.[12] Isolated OH groups in a hydrophobic matrix of EVOH are partly hydrated in liquid water or even in air. An OH acts as a donor to water in the hydrate of an isolated OH. This structure agrees with that of the hydrate complex in nitrogen,[8] but not with that in argon[9] or in the gaseous state.[7,11] In many theoretical studies of the hydrate complex of an alcoholic OH, mostly that of methanol, it has been reported that the hydrate structure, in which an alcoholic OH acts as an acceptor, is more stable than the other, in which an OH behaves as a donor, the energy difference between the two hydrate structures being about 1 kcal.[8,13−16] On the other hand, as mentioned above, experimental studies indicate that the stable structure of the hydrate complex of an isolated OH group changes, depending on the environment.

In a previous paper[2] we developed the hydrophobic isolation infrared spectroscopic method (HIIR) to study interactions of an organic molecule with water. Here we apply this method to study interactions of an isolated OH group with water, which coexists with associated OH groups, in a solution of 2-nonanol in heptane. We found that an isolated OH acts as a proton acceptor or a proton donor to water, depending on the concentration.

Experimental Section

Materials. 2-Nonanol (purity, >98%) and n-heptane (purity, >99%) were purchased from Tokyo Kasei Kogyo, Ltd. The compounds were used as received without further purification, and were dehydrated by 4 Å molecular sieves (Nacalai Tesque, Inc.) before use.

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Spectroscopic Measurements. The interaction of an isolated OH group with water in hydrophobic medium was investigated on the basis of the spectra obtained by the HIIR method.[2]

The original *nonhydrated* solutions were prepared from dehydrated 2-nonanol and heptane at concentrations from 0.05% (v/v) to 100% (or neat) in vials of 1 or 3 mL capacity. A spectrum of the nonhydrated solution (Sd) was measured in an OH-free quartz cell of 1 or 2 mm path-length. After the measurement, a small amount of water (50 or 100 μL) was added to the original solution in the vial. The mixture was vigorously stirred to ensure that it was saturated with water. After being stirred, the mixture was kept still for about 1 h, so that dispersed water particles coalesced to droplets at the bottom or the wall of the vial. A quantity of the *hydrated* solution was transferred with a pipet, with care not to include water droplets, from the vial into the same quartz cell that had been used to measure the Sd spectrum, and the spectrum (Sh) was measured. The spectral change caused by hydration of an OH group of 2-nonanol was detected as the difference spectrum between Sh and Sd (Sh−Sd). 2-Nonanol, which contains the long hydrocarbon moiety $CH_3(CH_2)_6CHCH_3$, was chosen as the carrier of an OH group, so that the hydrate complex was completely soluble in the solution in heptane but not soluble at all in dispersed water particles. The selection made it possible to separate even a very small change that was caused by hydration in the spectrum, by subtraction.

The Fourier transform infrared/near-infrared (FT-IR/NIR) spectrometer was a Nicolet Magna 760, equipped with a W-halogen lamp, a beam splitter of CaF_2, and a DTGS detector. The near-infrared and infrared spectra of a solution sample were measured with a resolution of 4 cm^{-1} and 200 scans in the 11000−2100 cm^{-1} region.

The amount of dissolved water was quantitatively analyzed by the Karl Fischer method[17] (Mitsubishi Chemical CA-06 type) for each hydrated solution sample, after its infrared/near-infrared spectra had been measured.

In what follows, the term "a *separated* spectrum" is used to denote the separated spectrum of 2-nonanol in the solution, in which the spectrum of the solvent (n-heptane) was subtracted from that of the solution with the subtraction factor of $1 - c$, c being the volume fraction of 2-nonanol in solution. Sometimes, the term "nonhydrated" or "hydrated" is attached to explicitly indicate whether the *separated* spectrum is of 2-nonanol in the solution before or after hydration, respectively, whereas the above-mentioned difference Sh−Sd is referred to as "a *difference* spectrum" hereafter.

Theoretical Calculation. The effect of hydration on the normal vibrations and absorption intensities were estimated by an *ab initio* quantum mechanical method, using 2-butanol (isobutyl alcohol) instead of 2-nonanol to reduce computational time. The hydrogen-bonded complex between 2-butanol and water was first constructed using the Gauss View program. The structure was optimized by the Gaussian 03W program with B3LYP method and 6-31G (d) basis set.

Normal frequencies and their absorption intensities were calculated for the optimized structures, using the Gaussian 03W program. The density-functional theory (the B3LYP functional) is implemented in the quantum mechanical method. The 6-31G(d) basis set was adopted, and the basis set superposition error (BSSE) was corrected by the counterpoise method. The frequencies thus obtained were finally multiplied by a scale factor of 0.9753.[18]

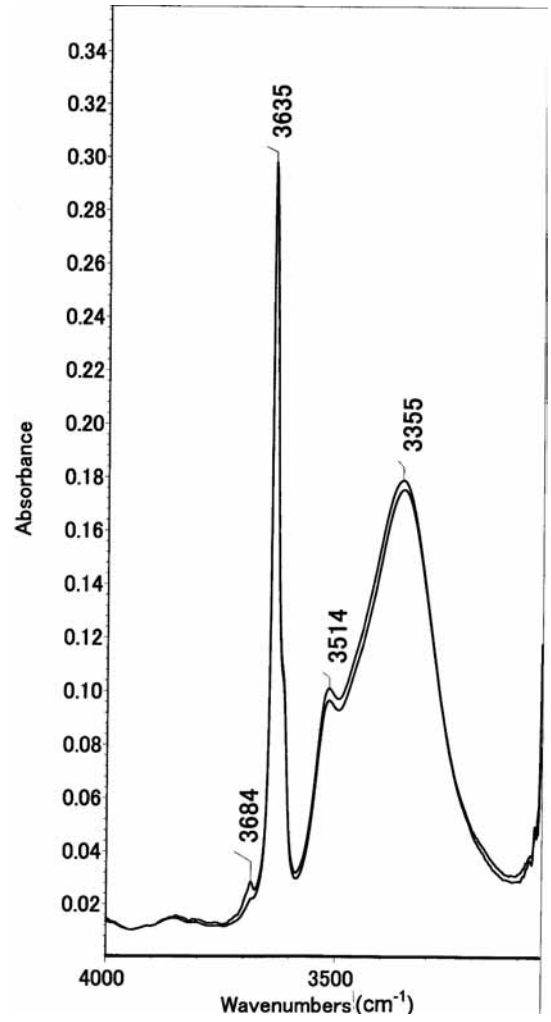

Figure 1. The separated spectra of 2-nonanol in (a) nonhydrated and (b) hydrated solution in heptane at 1.5% concentration, spectrum a being the one that is weaker at 3684, 3514, and 3355 cm^{-1}.

Results and Discussion

In the following discussion, "free OH" is used to denote the hydroxyl group of 2-nonanol that is free from being hydrogen-bonded to itself or to water. The term "isolated OH" is used to denote the OH that is free from being hydrogen-bonded to itself but is often hydrogen-bonded to water.

Dependence of the Difference Spectrum on Concentrations. Changes caused by hydration were investigated in the infrared and near-infrared spectra of 2-nonanol at various concentrations from 0.05% to 100% (v/v) in the solution in heptane. The *difference* spectra were significantly different between the concentrations below and above about 2%. The following discussion deals with the spectral features at the concentrations 1.5 and 5%.

Figure 1 shows the *separated* spectra a and b of 2-nonanol in the nonhydrated and hydrated states, respectively, at 1.5% concentration. In the spectrum a or b, a sharp band at 3635 cm^{-1} is assigned to a free OH, a weak one at 3514 cm^{-1} to oligomeric OH groups,[19,20] and a broader and strong one at 3355 cm^{-1} to associated OH groups. The absorptions around 3514 and 3355 cm^{-1} are slightly stronger in spectrum b, which is of 2-nonanol in the hydrated solution, than in spectrum a, which is of 2-nonanol in the nonhydrated solution. A very weak band appears at 3684 cm^{-1} in spectrum b only. The small differences between spectra b and a indicate that only a small proportion

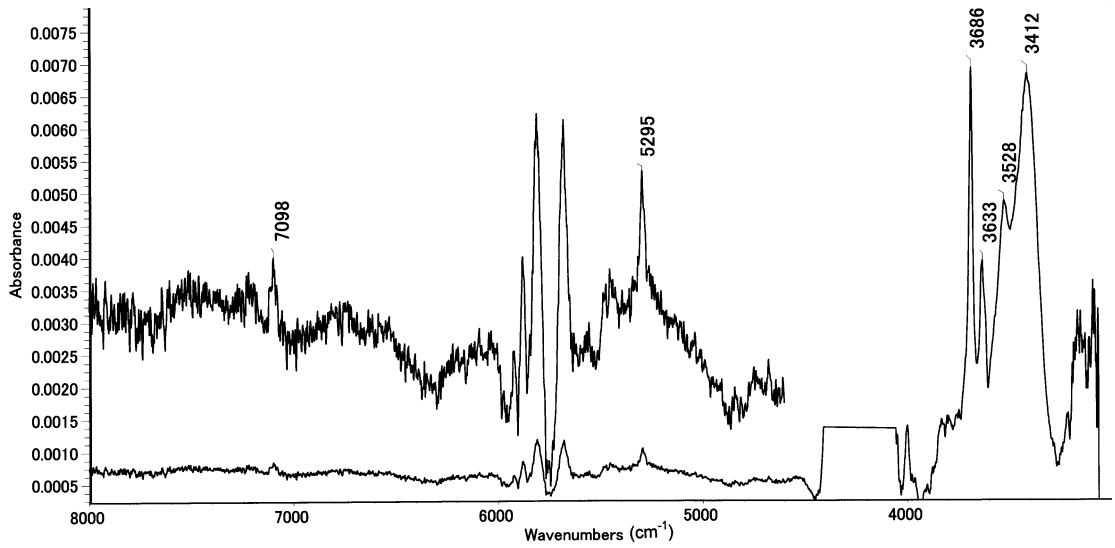

Figure 2. The difference spectrum in the 8000−3100 cm^{-1} region at 1.5% concentration. The upper spectrum is expanded by ten times against the given ordinate. The noise in the 4400−3900 and 6000−5500 cm^{-1} regions in the spectrum, the former being deleted, are caused by strong combination and overtone bands, respectively, of CH groups of heptane.

of OH groups is hydrated at this concentration in the hydrophobic solution.

We distinguished the small differences between the two spectra in Figure 1 in the difference spectrum shown in Figure 2. This spectrum shows four main peaks at 3412, 3528, 3633, and 3686 cm^{-1}. Only the last peak of these can be identified in the spectrum in Figure 1b before subtraction, but the others are recognized in the difference spectrum in Figure 2 only after the subtraction. This spectrum additionally shows very weak bands at 5295 and 7098 cm^{-1} in the near-infrared region. For convenience we designate these absorptions A, B, C, D, E, and F in the order of increasing frequency. The four infrared bands of A, B, C, and D appear in the *difference* spectrum also at the concentration of 0.6% as will be shown later, although they are much weaker. Band A does not appear at 0.3% concentration, at which the separated spectrum of 2-nonanol does not show any absorption around 3350 cm^{-1}, which is due to associated OH groups. This is clear evidence that band A should be assigned to the water, which is hydrogen-bonded to associated OH groups. Bands E and F are hardly observable at a concentration below 1.5%.

At this point we note that the C band at 3633 cm^{-1} actually has the same frequency as the OH stretching band of a free OH of 2-nonanol, as is seen from Figures 1 and 2. This means that appearance of the C band critically depends on the magnitude of the subtraction factor in the spectral processing. With this in mind, we performed the spectral subtraction with the subtraction factor of nearly or exactly 1.0. With careful processing, we confirmed that the C band reproducibly appears as a "plus" peak in the difference spectra, if the concentration was below about 2%. This suggests that the OH stretching band of an OH group may somehow change in absorption intensity by hydration.

Figure 3 shows the *separated* spectra a and b of 2-nonanol in the nonhydrated and hydrated solution in heptane, respectively, at 5% concentration. In spectrum a of 2-nonanol in the nonhydrated state, the band at 3353 cm^{-1}, which is assigned to associated OH groups, is much stronger than the sharp band at 3635 cm^{-1}, which is of a free OH. This spectral feature indicates that a majority of OH groups is associated at this concentration. Spectrum b of 2-nonanol in the hydrated solution, which shows a weak but clear band at 3684 cm^{-1}, is stronger than spectrum a in the spectral range except for a narrow region around 3635

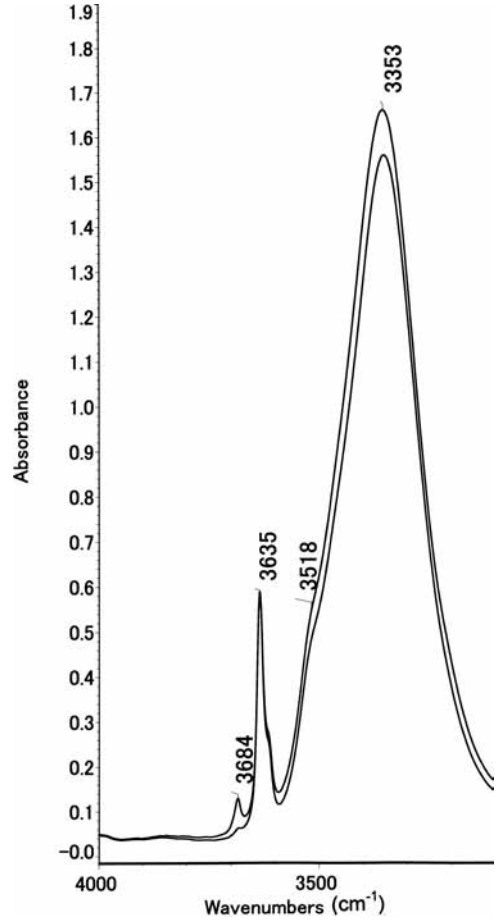

Figure 3. The separated spectra of 2-nonanol in (a) nonhydrated and (b) hydrated solution in heptane at 5% concentration, spectrum a being the one that is weaker at 3684, 3518, and 3353 cm^{-1}.

cm^{-1}. The change, which is caused by hydration, is rather small, and this indicates that most OH groups are not hydrated even at this concentration in the hydrophobic medium. As the concentration increases, the band around 3685 cm^{-1}, which is assigned to the water hydrogen-bonded to an isolated OH and corresponds to the band D in the difference spectrum, increases in intensity as expected, relative to the sharp band due to a free

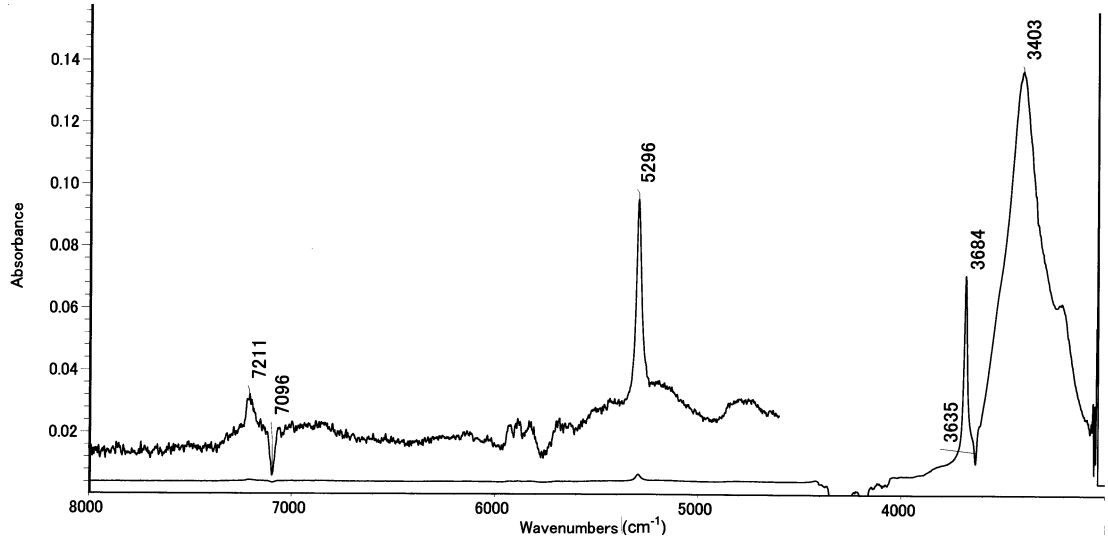

Figure 4. The difference spectrum in the 8000−3100 cm^{-1} region at 5% concentration. The upper spectrum in the 8000−4500 cm^{-1} region is expanded by 40 times against the given ordinate.

TABLE 1: Absorptions Caused by Hydration, Appearing in the Difference Spectra in Figures 2 and 4 at 1.5 and 5% Concentrations, Respectively

notation of bands	freq (cm^{-1})	concn: 1.5%	concn: 5%	assignments
A	3412	strong, broader	very strong, broader	water
B	3528	weak, sharp	nonobserved	water
C	3633	medium, sharp	"minus", weak	isolated OH
D	3686	strong, sharp	strong, sharp	water
E	5295	very, very weak	weak, sharp	water
F	7098	very, very weak	"minus", very weak	isolated OH
G	7211	nonobserved	very weak	water

OH at 3635 cm^{-1} in the corresponding *separated* spectra of 2-nonanol as in Figure 3b, for example, for the hydrated solution.

We subtracted the spectrum of the nonhydrated solution from that of the hydrated one with the subtraction factor of 1.0. The *difference* spectrum is shown in Figure 4. The absorptions in the spectrum, which are similar in frequency to those in Figure 2, are similarly denoted A, B, etc. The spectrum shows a sharp band at 3684 cm^{-1} (band D) and a strong band with a large bandwidth at 3403 cm^{-1} (band A). It is important to note that a "minus" peak appears at the frequency of band C or at 3635 cm^{-1}. No separate band appears at the frequency of the band B around 3530 cm^{-1} on the steep slope of the strong band at 3403 cm^{-1}. In the near-infrared region of the spectrum in Figure 4, band E is clear at 5296 cm^{-1}, and a weak "minus" peak appears at 7096 cm^{-1} or at the frequency of band F. A new weak band, denoted G, appears at 7211 cm^{-1} in the difference spectrum in Figure 4. As the concentration increases to 100%, band D increases in intensity, and bands C and F correspondingly increase in "minus" intensity in the difference spectra. At a concentration of 7% or above, band A is not separated as a clear band but is deformed by noise, because the band due to the associated OH groups around 3350 cm^{-1}, which overlaps the band A, rapidly intensifies with increasing concentration and is saturated at this concentration or above.

The spectral changes revealed in the difference spectra in Figures 2 and 4 are summarized in Table 1. The bands A, B, D, E, and G are assigned to the water that is hydrogen-bonded to an isolated or associated OH in the solution. The clear bands A, D, and E commonly appear in the spectra in Figures 2 and 4, but band B, which is clear in the spectrum in Figure 2, does not appear in the spectrum in Figure 4. Band G is observed only in the spectrum in Figure 4. In contrast, bands C and F, both of which have the frequencies of a free OH, appear in an opposite manner at the two concentrations, as discussed above. This observation indicates that the structure, in which an isolated OH is hydrogen-bonded to water, is different between the concentrations below and above about 2%.

Structure of the Hydrate Complex of an Isolated OH. Here we consider the hydrate structure of an alcoholic OH isolated in the hydrophobic solution, on the basis of bands B, C, D, E, and F in the difference spectra. Bands C and F of the isolated hydrated OH are particularly decisive in determining the structure, as will be discussed.

Here we assume that only one water molecule is hydrogen-bonded to an isolated OH group in the hydrophobic solution, as in the case of the hydrate complex of an ether O or ketone C═O in heptane.[2] The difference spectrum in Figure 2 or 4 may then be interpreted in terms of either one of the following two hydrate structures of an isolated OH,

$$HO\cdots H_b-O-H_f \quad \text{(I)}$$

$$OH\cdots OH_2 \quad \text{(II)}$$

where the subscripts b and f denote "hydrogen-bonded" and "free", respectively. In the hydrate structure of I, the OH acts as a proton acceptor to the water, which has nonequivalent H_b-O and $O-H_f$ bonds. The water should have different OH stretching frequencies, which are denoted as $\nu(OH_b)$ and $\nu(OH_f)$, respectively. In contrast, in the structure of II, the isolated OH acts as a proton donor to the water, which is symmetric. This water should have symmetric and antisymmetric OH stretching modes, which are denoted as $\nu_s(OH)$ and $\nu_a(OH)$, respectively. In what follows, we pay particular attention to why a "plus" or "minus" peak appears at the frequencies of the OH stretching and its overtone of a free alcoholic OH.

It is known that the effect of hydrogen bonding on the vibrational property of an alcoholic OH is significantly different between OH(D) and OH(A) in the one-to-one hydrogen-bonded OH(D)···OH(A) pair in a diol, where D and A denote a donor and an acceptor, respectively.[21−26] In what follows, we assume that an OH of water, which is similar in nature to an alcoholic

TABLE 2: Calculated Frequency and Intensity of the OH Stretching Vibration of a Free and Hydrated OH of Isobutyl Alcohol

	free OH	OH in HO···H_b−O−H_f
ν(OH) (cm^{-1})	3740	3741
intensity	5.5	14.1

TABLE 3: Assignments of the Three Bands in the 4000−3500 cm^{-1} Region in the Difference Spectrum in Figure 2

obsd freq (cm^{-1})	assignments to the vibrations of HO···H_b−O−H_f
3633	ν(OH) of OH
3528	$\nu(OH_b)$ of water
3686	$\nu(OH_f)$ of water

OH, has an influence similar to that of an alcoholic OH on the vibration of the alcoholic OH in the hydrate structures of I and II. That is, the vibrational frequency of an acceptor OH as in I is not affected by the hydration, but that of a donor OH as in II is significantly shifted downward.

First we interpret the difference spectrum in Figure 2, which shows a "plus" peak at 3633 cm^{-1} and a sharp peak at 3686 cm^{-1}. From its frequency,[20] the former band should be assigned to the isolated OH that is hydrated, and the latter is definitely assigned to the water that is hydrogen-bonded to the OH,[2] because this band appears only after hydration as in the spectrum in Figure 1b. Appearance of the former band at the same frequency as a free OH suggests that the OH in the hydrate acts as an acceptor as in I, because otherwise the band should be shifted down,[25] and this shift should give rise to a "minus" peak at the frequency of a free OH in the difference spectrum. Instead, appearance of the "plus" peak there implies that the hydration has the effect of enhancing the band of the alcoholic OH without any significant frequency change. To theoretically investigate the implication, we quantum-mechanically calculated the frequency and intensity of the stretching band of an OH that acts as an acceptor in the hydration, and of a free OH for isobutyl alcohol. The results are given in Table 2. According to the table, the hydration does not actually affect the frequency, in agreement with the above assumption, but significantly increases the intensity of the OH stretching band of the acceptor OH. The theoretical result is consistent with the above assignment of the *plus* band at 3633 cm^{-1} to the alcoholic OH in the hydrate structure of I. Correspondingly, the water in the hydrate structure is expected to have the two bands of $\nu(OH_f)$ and $\nu(OH_b)$ modes. The band of a higher frequency at 3686 cm^{-1} is assigned to the stretching band of the free OH or $\nu(OH_f)$, whereas the one of a lower frequency at 3528 cm^{-1} is assigned to that of the hydrogen-bonded OH or $\nu(OH_b)$. The assignment is reasonable, in comparison with the frequencies of 3694 and 3509 cm^{-1} for the $\nu(OH_f)$ and $\nu(OH_b)$, respectively, of the O···H_b−O−H_f of the hydrate complex of an ether O.[2] The assignments of the three absorptions in the 3700−3500 cm^{-1} region are summarized in Table 3, and we conclude that the hydrate of an isolated OH has the structure of I at a concentration below about 2% in the hydrophobic solution in heptane.

Next we consider the spectral feature that "minus" peaks appear at the frequencies of the OH stretching and its overtone bands of a free OH in the difference spectrum in Figure 4. If an isolated alcoholic OH acts as a *donor* in the hydration as in II, its stretching band should be shifted downward, just like a donor OH in a hydrogen-bonded OH pair.[21−26] This should cause a decrease in intensity at the frequency of the OH stretching of

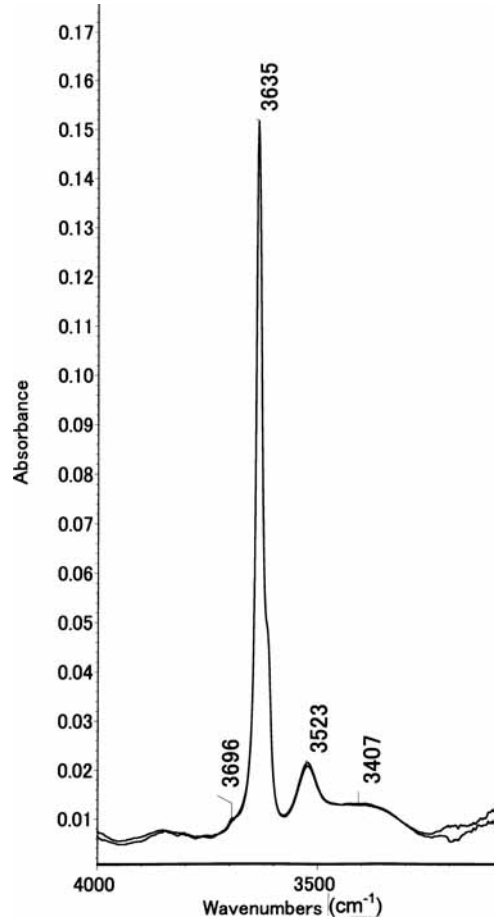

Figure 5. The separated spectra of 2-nonanol in (a) nonhydrated and (b) hydrated solution in heptane at 0.6% concentration, spectrum a being the one that is very slightly weaker at 3686 and 3523 cm^{-1}.

a free OH. The decrease is expected to result in a *minus* peak at the frequency in the *difference* spectrum, in which the spectrum of the nonhydrated solution is subtracted from that of the hydrated one. The same should also occur at the frequency of its overtone band. What is expected above for the hydrate structure of II is just the observed feature that *minus* peaks appear at 3635 and 7096 cm^{-1} in the difference spectrum (Figure 4). Thus, the observation provides definite evidence that the hydrate structure of II occurs at a concentration above about 2%. However, it should be noted that a band due to the donor OH, which is expected to appear in the 3550−3500 cm^{-1} region, is concealed in the steep slope, produced by the minus peak, of the strong peak at 3403 cm^{-1}.

The symmetric water in the hydrate structure of II should have the two bands of ν_s(OH) and ν_a(OH). A sharp band at 3684 cm^{-1} in the spectrum in Figure 4 is definitely assigned to the ν_a(OH) band from its high frequency.[12]The frequency is lower by 30 cm^{-1} than the frequency 3713.8 cm^{-1} of the ν_a(OH) mode of the water in the CH_3OH(donor)···OH_2(acceptor) complex deposited on a CsI window at low temperature.[8] The shift is considered to be caused by matrix and temperature effect. It is noted that the ν_a(OH) band of the symmetric water in II happens to have the same frequency as the $\nu(OH_f)$ band of the asymmetric water in I. The band of the ν_s(OH) mode, which is expected to appear in the 3600−3500 cm^{-1} region, is not separated, probably because it is disturbed by the steep slope caused by the *minus* peak at the high-frequency side of the 3403 cm^{-1} band. The spectrum in Figure 4 shows two additional bands at 5296 and 7211 cm^{-1} of the water. The former band,

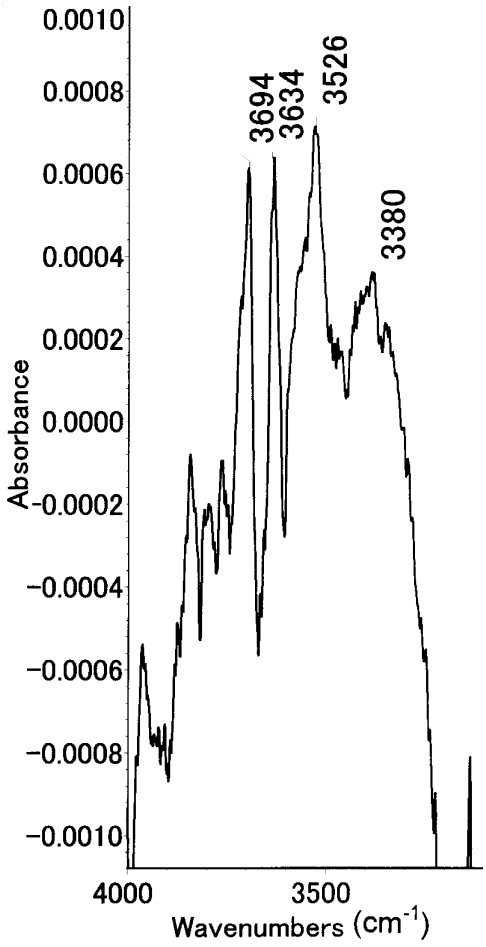

Figure 6. The difference spectrum in the 4000−3100 cm^{-1} region at 0.6% concentration.

which is clear and sharp, is assigned to the first combination band of the antisymmetric stretching and deformation (denoted as δ(OH)) or ν_a(OH)+δ(OH),[12,27] and the latter is assigned to the first overtone of the antisymmetric OH stretching or [$2\nu_a$(OH)].[28] According to our previous study,[27] a symmetric water as in II shows only one combination band of the ν_a(OH)+δ(OH) mode, whereas an asymmetric water as in I shows two combination bands of the ν_f(OH)+δ(OH) and ν_b(OH)+δ(OH) modes. The appearance of only one combination band at 5296 cm^{-1} in the difference spectrum in Figure 4 indicates that the water is symmetric as in II but not asymmetric as in I.

Stability of Hydrate Structure. As explained above, the hydrate of the structure of I exists in a narrow concentration range only below about 2%, whereas that of II exists at a concentration above this up to 100%. We should add that an isolated OH is not hydrated at all at a concentration below about 0.3% in the solution, although a small amount of water is dissolved even at such a low concentration.[2,29] The observation suggests that the hydrate complex is not stable at such a low concentration in the strongly hydrophobic medium, in which an OH group is almost totally free.[30] The sharp D band of the water in the hydrate structure of I is very weak with a peak at 3696 cm^{-1} in the difference spectrum at the concentration of 0.3%, and as the concentration increases above this, the frequency gradually shifts down to 3686 cm^{-1} at 1.5% concentration, as in the spectrum in Figure 2.

To demonstrate the observation at very low concentrations, we consider what was observed at 0.6% concentration. Figure 5 shows the separated spectra of the OH of 2-nonanol in the nonhydrated and hydrated solutions at this concentration. The two spectra are almost identical. The band at 3635 cm^{-1}, which is assigned to a free OH group, is much stronger than the one at 3523 cm^{-1}, which is assigned to an oligomeric OH group.[19,20] Another very weak and broad band around 3400 cm^{-1} is assigned to associated OH groups. This spectral feature indicates that most of OH groups are free, a small fraction of them is oligomeric, and an even smaller fraction of them is associated at this concentration. Spectrum b, which is of 2-nonanol in the hydrated solution, shows a barely recognizable weak peak at 3696 cm^{-1}, which is of the water hydrogen-bonded to an isolated OH. This weakness of the band indicates that only a very small fraction of free OH groups is hydrated in the strongly hydrophobic solution. The spectrum of the hydrated part is separated by subtraction, as shown in Figure 6. This spectrum, in which the signal-to-noise level is low, is sufficiently well resolved to show the weak bands of B, C, and D, which were assigned to the hydrate structure of I, as discussed above. It should be noted that band D, which is of the $\nu(OH_f)$ mode of the partner water, has a higher frequency of 3694 cm^{-1} at this concentration, as mentioned above. The band at 3634 cm^{-1}, which is of the ν(OH) mode of the hydrated OH, and the one at 3526 cm^{-1}, which is of the $\nu(OH_b)$ of the water, have actually the same frequencies as described in Table 1. Thus, only the D band of the water shifts upward with decreasing concentration. The deformed band at about 3400 cm^{-1} is that of the water contained in a small amount in associated OH groups, and this band disappears at

TABLE 4: Molar Fraction of Free OH in the Solution of 2-Nonanol in Heptane at Various Concentrations and Its Hydrated Fraction

concn (%(v/v))	molar fraction of free OH[a]	hydrated fraction of free OH[b]
1.2	0.82	0.003
1.5	0.73	0.007
2.0	0.65	0.010
3.0	0.54	0.018
5.0	0.40	0.034
10	0.26	0.069
30	0.10	0.16
50	0.07	0.30
70	0.05	0.40
100	0.04	0.54

[a] The molar fraction of free OH at a concentration was determined from the peak-height intensity of the band at 3635 cm^{-1} of a free OH relative to the expected intensity at the concentration from its molar peak-height intensity. [b] The hydrated fraction of free OH was estimated as [$1 - (P_{3635}^h/P_{3635}^d)$] at a concentration of 3% or more, where P_{3535}^h and P_{3635}^d denote the peak-height intensity of the band at 3635 cm^{-1} after hydration and that before hydration, respectively. However, at the concentration of 2% or less, it was not possible to determine the hydrated fraction of free OH in the same manner. To tentatively estimate the fraction, we assumed that the molar peak intensity of the OH stretching band of a *donor* water at about 3685 cm^{-1} is equal to that of the antisymmetric OH stretching band of an *acceptor* water. Then, we changed the observed peak-height intensity of the band of the water to that of a free OH on the basis of the molar peak-height intensity ratio, which is obtained at a concentration above 3%, of the band of a free OH to the ν_a(OH) band of an acceptor water. The hydrated fraction of free OH was then calculated as the ratio of the intensity thus obtained to the observed peak-height intensity of free OH, the enhancement of the band by hydration being negligible at such a small hydration. The estimation was not possible at the concentration of 0.9% or less, because the band of water around 3690 cm^{-1} appears only as an obscure swelling before subtraction, although the band of water was separated in the difference spectrum.

0.3% concentration, where the band of associated OH groups is negligibly weak.

The frequency shift observed of the $\nu(OH_f)$ band, depending on the concentration, suggests that the hydrate structure of the isolated OH may slightly change even within the narrow concentration range below about 2% in the hydrophobic solution. The observation suggests that, as the concentration of the solution increases, the hydrate structure of I becomes unstable at about 2% concentration, and instead the structure of II emerges.

Table 4 shows the molar fraction of a free OH and its hydrated fraction at various concentrations above 1.2% at room temperature in the solution of 2-nonanol in heptane. The fraction of free OH groups rapidly decreases, as the concentration increases. A nonanol OH group should dynamically change from free to associated in solution in n-heptane.[31,32] As the concentration of 2-nonanol increases in the solution, the time during which an OH group is free in hydrophobic solution should become shorter than the time during which it is hydrogen-bonded to neighboring OH groups. Thus, the time-averaged property of an isolated OH should change depending on the concentration of 2-nonanol in the solution. As a result, an isolated OH tends to be more hydrated, as the concentration increases, as is seen from Table 4. The changing property of an isolated OH, which depends on the concentration, is considered to influence the stability of the hydrate complex in the solution so as to produce the hydrate structure of II at a concentration above about 2%.

Conclusion

In the present paper we studied the structure of the hydrate complex of an isolated OH of 2-nonanol in heptane. An *isolated* OH, which can act as a proton acceptor or a proton donor, is hydrogen-bonded to water in two different manners. The hydrate structure of I, in which an OH acts as an acceptor to water, is stable only in a narrow concentration range from 0.3 to about 2%. In contrast, the hydrate structure of II, in which an OH is hydrogen-bonded as a donor to water, is stable in a broad concentration range from about 2% up to the neat. The hydrate structure of I, which occurs in a narrow concentration range below about 2%, agrees with the structure previously reported in many experimental studies.[7,9,11] In addition, theoretical studies have reported that the structure of I is more stable than that of II.[13−16] On the other hand, the structure of II, which occurs in a broader concentration range above about 2%, agrees with the structure found in a nitrogen matrix[8] and in EVOH.[12] In the latter case of EVOH, an OH, which is isolated in the hydrophobic ethylene matrix similar to the hydrophobic medium of heptane in the present study, is hydrated as a donor to water at about 10%(mol) concentration of vinyl alcohol or more.[12] Thus, occurrence of the hydrate structure of II above 2% concentration in the hydrophobic solution is consistent with what was found for the hydrate of the isolated OH in EVOH.[12]

The present study provides basic data for the understanding of complicated interactions of water with associated OH groups, which are of much importance for chemistry. A combined experimental and theoretical approach is indispensable for resolving complicated interaction mechanisms of water in associated OH groups, especially because it is difficult to analyze contributions of OH groups and water to the broadened strong infrared absorption observed. Previous studies strongly suggest that water and alcoholic OH combine to form hydrogen-bonded networks in associated OH groups.[10,12,33]

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(28) The frequency of 7211 cm^{-1} is approximately two times the fundamental frequency ($2 \times 3684 = 7368$). The discrepancy of 157 cm^{-1}, which is caused by anharmonicity possessed by the vibration, is similar to that (174 cm^{-1}) for a free OH ($2 \times 3635-7096 = 174$). The above assignment is reasonable, because the OH of water is similar in nature to that of an alcoholic OH.

(29) Solubility of water was about 0.003% in weight even at a concentration below 0.3%, and the solubility continues to be nearly the same until a concentration of about 1% in a solution of 2-nonanol in heptane.

(30) The fraction of an isolated (or free) OH was more than 0.99 at a concentration of 0.3% (v/v) or less in a solution of 2-nonanol in heptane.

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