

Basic Interactions of Water with Organic Compounds

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In the present report we have studied the interactions of water with organic molecules possessing a functional group of an ether or a carbonyl group in solution in a hydrophobic medium or *n*-heptane at various concentrations. The infrared spectrum of the water in the water–organic molecule complex, which was clearly separated by a skillful subtraction method, drastically changed depending on the concentration of the solution. Analysis of the infrared spectrum has made clear the following. Water is hydrogen-bonded, by one OH only, to a functional group, with the other OH free, to form a *one-bonded* complex, when a functional group is isolated from the other in the hydrophobic medium. On the other hand, each OH of a water molecule is hydrogen-bonded to a functional group to form a *two-bonded* complex, when two or more of the group are within the interactive vicinity via water. The hydrogen-bonding structure of the complex was supported by the normal frequencies calculated by the *ab initio* quantum mechanical method. The present study has demonstrated that the *hydrophobic isolation* method combined with *infrared spectroscopy* (HIIR) is useful to study basic interactions of water with organic molecules under soft conditions.

Introduction

To understand the role of water in chemistry and in life, it is important to study the interactions of water with organic and polymeric materials at the molecular level. It is well-known that water interacts with organic or polymeric molecules through hydrogen-bonding.^{1,2} Infrared spectroscopy is one of most powerful methods to study the interactions,^{3–6} since not only the frequency and the shape of the OH stretching absorption of water are very sensitive to the interactions but also recent Fourier transform infrared (FT-IR) spectroscopy has been so developed as to separate delicate spectral differences.⁷ Many studies have been made of the infrared spectra of water in solution or in liquids^{5,8–13} or in polymers.^{14,15} Water shows complicated infrared spectra depending on the medium^{5,9,11–13} in which it is dissolved. When water composes a major component in solution, the infrared spectrum is characterized by the absorptions caused by complicated interactions among the water molecules themselves.^{5,9,11} Even when water is a minor component,^{12,13} the infrared spectrum significantly changed from in one compound to in the other. An attempt was made to analyze the varying infrared spectra of the water dissolved by peak separation, to report that there were some kinds of hydrogen-bonded clusters.^{12,13} The basic interacting picture of water with organic molecules still remains unclear. On the other hand, the interactions of water with gases were studied on the surface of ices.^{16–19} It was reported that free OH groups, which have high OH stretching frequency, exist on ice surfaces.^{16,18}

One of the authors (H.K.) reported that water dissolved in polymers showed two well-defined OH stretching absorptions and that their frequencies shifted down as a polymer, in which water was dissolved, became more hydrophilic.^{14,15} Another author (R.I.) has been studying the interactions of water with various polymers by following the spectral change during dehydration by the use of FT-IR spectroscopy.^{20,21} In the course

of the study he found that the water in some ethylene copolymers showed those *unusual* three OH stretching absorptions, whose relative intensities drastically depended on the ethylene composition.²² He thought that the hydrophobic portion or the ethylene component should have a crucial effect on the spectral changes of water. In the present study, as the medium to interact with water we chose the solution of an organic compound in a hydrocarbon solvent, where the composition and a functional group, which is to interact with water, can be freely changed, instead of the ethylene copolymers. Analysis of the infrared spectra of the water in the hydrate complex at various concentrations has revealed the most basic interacting patterns of water with organic molecules.

Method

Here let us describe the developed method, by which the spectrum of the water in the complex between water and an organic molecule is selectively observed. First, we select an organic molecule, which consists of a functional group that is to interact with water and of a moderately long hydrocarbon chain. This is denoted as a carrier molecule, hereafter, for convenience. The hydrocarbon part of the carrier molecule is to make the hydrate complex “soluble” only in a hydrophobic solvent but “not soluble at all” in the water phase. This requirement, which is to keep constant the composition of the hydrophobic solution even after mixing with excessive water, is needed to excellently cancel the absorptions of the solution by subtraction to separate the absorptions of the water in the complex, even if they are very weak.

The practical procedure of the method is as follows. First, the carrier molecule is dissolved in a hydrophobic medium at a concentration. This solution is denoted as P, for convenience. Second, a small but excessive amount of water is mixed into the solution in a small vial. The mixture is vigorously stirred by shaking, so that water is in sufficient contact with the carrier

molecule to produce the "hydrate complex" at saturation. Here, we denote the hydrophobic solution that contains the complex as Q. Then, the infrared spectrum of the water in the complex is separated by subtracting the spectrum of P from that of Q. The infrared spectrum of the water in the complex in the solution should be well separated to very weak absorptions.

In this method it is possible to change the environment of a carrier molecule that is to interact with water, from neat to the state in which the carrier molecule is sufficiently isolated beyond the interactive vicinity of the neighbor via water in the solution. This makes it possible to observe the water that is hydrogen-bonded to a carrier molecule in various manners. In practice we measured the spectrum in the 10000–2000 cm^{-1} region by the use of an OH-free quartz liquid cell of 1 or 2 mm thickness. The use of the liquid cell of that thickness made it extremely easy to carry out sample preparations for the spectral measurements. In the present report the fundamental absorptions of the OH stretching of water in the 4000–3000 cm^{-1} region only were discussed, although the absorptions of the overtones and combinations of water also have useful structural information.

The key point of the present method is the *isolation* of the hydrogen-bonded complex with water in *hydrophobic* medium and the separation of the *infrared* spectrum of the water in the complex by the subtraction of the spectrum of the solvent. This method is named as *hydrophobic isolation infrared spectroscopy* or simply as HIIR.

Experimental Section

Materials. The carrier molecules chosen in the present study were di-*n*-butyl ether [$\text{CH}_3(\text{CH}_2)_3\text{O}(\text{CH}_2)_3\text{CH}_3$] (BE) (purity, 99%; Nacalai Tesque, Ltd.), di-*n*-octyl ether [$\text{CH}_3(\text{CH}_2)_7\text{O}(\text{CH}_2)_7\text{CH}_3$] (OE) (purity, >95%; Tokyo Kasei Kogyo, Co. Ltd), and 3-decanone [$\text{CH}_3(\text{CH}_2)_6\text{COCH}_2\text{CH}_3$] (3DN) (purity, >96%; Tokyo Kasei Kogyo, Co. Ltd). The hydrophobic solvent used in the present study was *n*-heptane (purity, >99%; Tokyo Kasei Kogyo, Co. Ltd.). All the chemicals were used as received without further purification. All the compounds used in the present experiment were dehydrated by Molecular Sieves of 4A (Nacalai Tesque, Ltd).

Spectroscopic Measurements. The solution of a carrier molecule in *n*-heptane was prepared at a concentration from neat to 5% (v/v) in a vial of 1.0 mL. The infrared spectrum of the P solution was measured at first. After the measurement, a quantity of water (50 μL) was dropped into the solution and was vigorously stirred, the excessive water being precipitated as small drops on the wall or at the bottom. After the mixture was allowed to stand for about 30 min for the sufficient precipitation of water droplets, an amount of the Q solution that contains the water–carrier molecule complex was carefully taken from the mixture by a pipet into a quartz cell for the spectral measurement and the infrared spectrum was measured. The same quartz cell of 1 mm (or sometimes 2 mm) thickness was used for the spectral measurements of the P and Q solutions at a concentration of a carrier molecule. The spectrum of the water in the complex was obtained by subtracting the spectrum of P from that of Q with a subtraction factor of 1.0 in most cases.

The infrared spectra were measured with a resolution of 4 cm^{-1} and 50 scans (or sometimes 200 scans) by the use of a Nicolet Magna 760 FT-IR spectrometer, equipped with a W-halogen lamp, a beam splitter of CaF_2 , and a DTGS detector. Especially to improve the S/N ratios of the very weak absorptions of the water in pure *n*-heptane, the spectra of *n*-heptane itself and the solvent saturated with water were measured with 200 scans by the use of a quartz cell of 2 mm thickness.

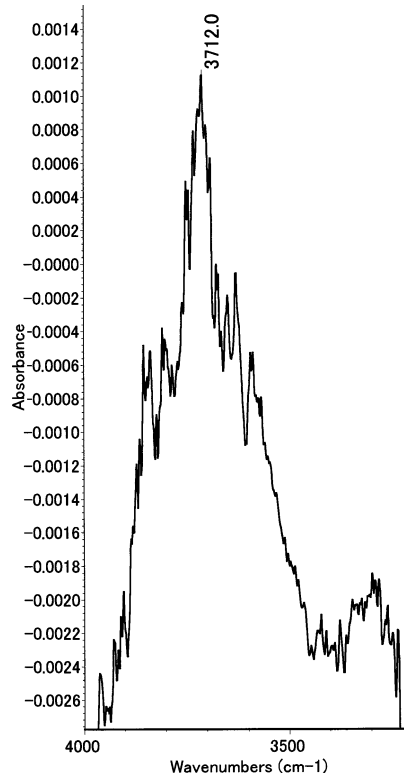


Figure 1. Infrared spectrum of the water dissolved in *n*-heptane.

The solubility of water in the Q solution was determined by the Karl Fischer method (Mitsubishi Chemical CA-06 type) for the same solution, of which the infrared spectrum was measured.

Calculation of Normal Frequencies. The frequencies of the normal vibrations were calculated by the *ab initio* quantum mechanical method for the water molecule in the complex, which will be proposed below. The structure of the complex was first constructed on the basis of the coordinating structure of the hydrate complex. The structure optimization and calculation of the normal frequencies were performed by the Gaussian 98W program with the B3LYP method and the 6-31G(d) basis set. The original values thus obtained were multiplied by a scaling factor of 0.9753 to give the calculated frequencies.

Results and Discussion

In the present experiment *n*-heptane was found to be appropriate for the hydrophobic medium. *n*-Heptane does not have any severely interfering absorptions in the frequency 10000–3000 cm^{-1} region except in the 4500–4000 cm^{-1} region, where there appears a group of strong absorptions due to the first combinations of the CH stretching and CH deformation vibrations.^{23,24} The absorptions of *n*-heptane in the 4000–3000 cm^{-1} region can be sufficiently well canceled by subtraction. The absorptions of the water in the hydrate complex were well separated not only for the OH stretching bands in the 4000–3000 cm^{-1} region as in the present paper but also for the combination and overtone bands, which appear around 5200 and 7200 cm^{-1} , respectively, in the region above 4000 cm^{-1} .²⁵ In addition, *n*-heptane is not so viscous that the excessive water precipitates as small droplets in an appropriately short time.

n-Heptane itself dissolves a very small amount of water (Table 3). The separated spectrum of the OH stretching absorption of the dissolved water in *n*-heptane, which was obtained by subtraction just as in the solution of a carrier molecule, is shown in Figure 1. The absorption, which has such a high frequency as 3712 cm^{-1} , is considered to be assigned to the antisymmetric

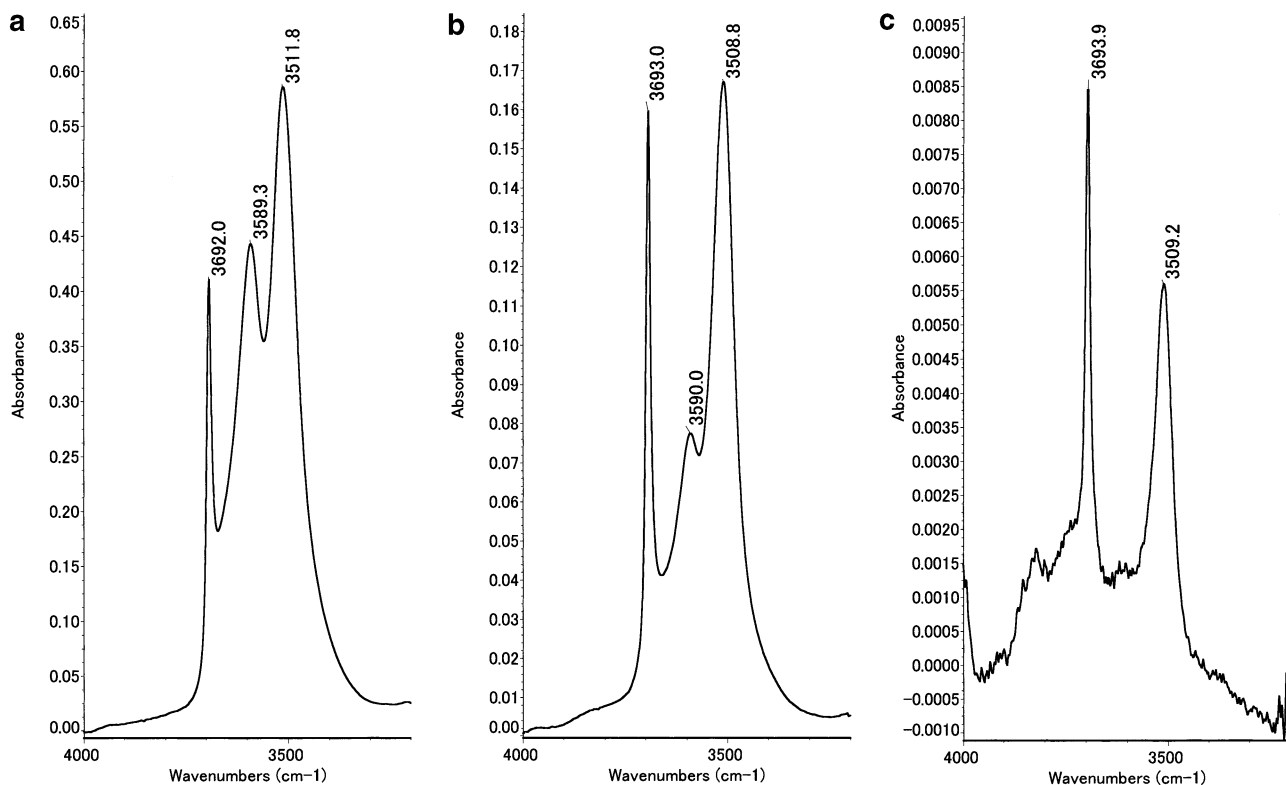


Figure 2. Infrared spectra of water dissolved in the solution of BE in *n*-heptane at the concentrations (a) 100 (neat), (b) 50, and (c) 5% (v/v).

OH stretching mode of a water molecule, although the one due to the symmetric mode cannot be recognized in the spectrum. The absorption, which has a large width, is very weak with an absorbance, in peak height, of totally about 0.004. The high-frequency of the peak and the low solubility indicate that the interactions between *n*-heptane and water are so weak that the water is molecularly dissolved by van der Waals interactions.⁸ The weak and rather obscure absorption of the water dissolved in *n*-heptane little interferes with observing the clear absorptions of the water in the hydrate complex with a carrier molecule, as will be seen later.

Figure 2 shows the infrared spectra of the dissolved water in the solution of BE in *n*-heptane at the concentrations 100 (neat), 50, and 5% (v/v). The spectra have three absorptions, which are denoted as A, B, and C from the high frequency side, for convenience. Their relative intensities drastically depend on the concentration of BE in the solution. According to the spectrum in Figure 2a, the water dissolved in the neat BE has the A, B, and C bands at 3692, 3589, and 3512 cm⁻¹, respectively. The C band is the strongest, and the B band is between the A and C bands in intensity. By contrast, the A band, which is the weakest among the three, is much sharper than the other two. At the concentration of 50%, the A band becomes even stronger relative to the C band, while the B band becomes much weaker. At the concentration of 5%, only A and C bands are distinct, and the B band becomes so weak that it cannot be recognized as a peak at the frequency, as in Figure 2c. According to the spectrum in Figure 2c, there appear some obscure swellings at the high-frequency side of the 3694 cm⁻¹ band. These may be due to the water dissolved in *n*-heptane, in reference to the intensity and the shape of the absorption shown in Figure 1. This demonstrates that the absorption of the water dissolved in the *n*-heptane component does not seriously interfere with the observation of the clear absorptions of the water in the hydrate complex even for the case where the absorption intensity of this is so weak as to be about 0.007 in absorbance in peak-

TABLE 1: Frequencies of the OH Stretching Absorptions for Water Dissolved in the Solution of BE, OE, and 3DN in *n*-Heptane^a

carrier molecule	conc [% (v/v)]	A (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)
BE	100	3692m	3590s	3511vs
	50	3693s	3590w	3508s
	5	3694vs	n.o.	3509s
OE	100	3690m	3587m	3504vs
	50	3692s	3589vw	3506s
	10	3693vs	n.o.	3508s
3DN	100	3688w	3625s	3543vs
	50	3692s	3638m	3550vs
	10	3696vs	n.o.	3558s

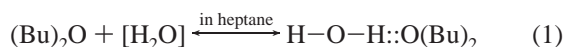
^a In this table the relative intensity of a band is given as very strong (vs), strong (s), medium (m), weak (w), or very weak (vw) among the three in a spectrum, and a nonobserved band is denoted as n.o.

height, as in Figure 2c. It should be noted that the intensity of the C band in peak-height as a representative decreases from 0.57 in absorbance at 100% to 0.0051 at 5%.

The water dissolved in the solution of the other carrier molecules in *n*-heptane similarly shows the three bands as in the BE solution. Their absorptions are listed in Table 1. Their relative intensities similarly depend on the concentration of the carrier molecules in the solution. It should be noted that the A band has such a high frequency as 3688–3696 cm⁻¹ independent of whether a functional group is an ether or a carbonyl. By contrast, the frequencies of the B and C bands depend on the chemical structure of a functional group. It should be added that the C band of the water in the solution of OE and 3DN, as a representative of the three, decreases in intensity just as in the BE solution, as the concentration decreases.

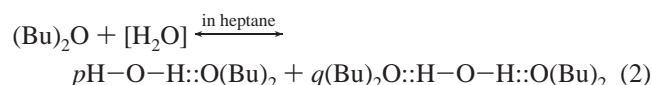
In the following let us consider what occurs for the water dissolved in the solution of BE as a representative, from the infrared absorptions depending on the concentration, also referring to the observed absorptions of the water in the OE and 3DN solution in Table 1.

It is important to note the following three points: (1) the absorption (representatively of the C band) of the water dissolved decreases in intensity as the concentration of BE decreases, as in Figure 2, and is not observed at all in *n*-heptane itself, as in Figure 1; (2) the A band has a high frequency of about 3700 cm⁻¹, independent of functional groups, as in Table 1; and (3) the C band, which is the counterpart of the A band at a low concentration, depends in frequency on the chemical structure of a functional group. The first point suggests that the water that shows the C band is practically not dissolved at all without being hydrogen-bonded to a functional group of a carrier molecule. The second and third points suggest that at a low concentration the water that shows the A and C bands is hydrogen-bonded, by one OH only, to a functional group, with the other OH free, to form the “one-bonded” complex of H—O—H::O(Bu)₂, where Bu is (CH₂)₃CH₃. For the water in the complex of this type, the OH stretching vibration should have different frequencies for the “free” and “bonded” OH groups, the vibrational modes of which are denoted as ν_f and ν_b , respectively. The ν_f mode should be independent of a functional group. The A and C bands in Figure 2c should be assigned to ν_f and ν_b , respectively. The complex formation of water with BE in the solution at a low concentration is then expressed as



The liquid water, which interacts with (Bu)₂O only during the “vigorous stirring”, remains in a separate phase after the stirring, and it is contained in a bracket in the formulation. *n*-Heptane, as the hydrophobic medium, plays a crucial role to “isolate” the complex or H—O—H::O(Bu)₂. The idea of the formation of the “one-bonded” complex leads to the interpretation of all the spectra of the water in Figure 2, as follows.

At a higher concentration of BE in the solution, a population of the “one-bonded” water dissolved should be surrounded by additional BE molecules in the interactive vicinity, to form the complex (Bu)₂O::H—O—H::O(Bu)₂, in which the water is “two-bonded”, as below,



where *p* and *q* are the populations of the one- and two-bonded complexes, respectively. In the “two-bonded” complex, the water molecule, the two H atoms of which are equivalent, should have symmetric and antisymmetric OH stretching modes, which are denoted as ν_s and ν_a , respectively. Their frequencies should characteristically depend on the strength of the hydrogen-bonding of a water molecule to a functional group. The B and C bands, whose frequencies depend on a functional group (Table 1), are assigned to the ν_a and ν_s modes, respectively. The one- and two-bonded complexes should coexist in the solution above the concentration at which the probability that one carrier molecule is within the interactive vicinity via hydrogen bonding to the neighbor is larger than a critical value. The population ratio of the two complexes or *q/p* should increase with the increasing concentration of BE. However, the bulky Bu group of BE that is hydrogen-bonded to one OH should hinder the free approach of another BE to the other OH, so that a population of the one-bonded complex should remain without being two-bonded even in the neat liquid. This is just what is observed for the spectrum in Figure 2a.

The formation of the one- and two-bonded complexes according to the above formulations reasonably explains the

TABLE 2: Comparison of the Observed Frequencies with the Calculated Ones of the OH Stretching Vibrations for the One- and Two-Bonded Water Molecules for the Carrier Molecules of BE and 3DN^a

carrier molecule		ν_f (cm ⁻¹)	ν_a (cm ⁻¹)	ν_s (cm ⁻¹)	ν_b (cm ⁻¹)
BE	obs	3694	3590	3511	3509
	calc	3708	3616	3539	3522
3DN	obs	3697	3638	3543	3563
	calc	3713	3637	3556	3557

^a The observed values of ν_a and ν_s were taken from the B and C bands, respectively, of water at 100%, while those of ν_f and ν_b were taken from the A and C bands, respectively, at the lowest concentration.

observed dependence of the spectra of the water dissolved on the concentration of BE, as shown in Figure 1. According to Table 1, the B and C bands of the water dissolved in the OE solution have nearly the same frequencies as those in BE. This is reasonable since the functional group which the water is hydrogen-bonded to is an ether O atom for both BE and OE. The relative intensity of the B band to the C band of the water dissolved is significantly smaller in the neat OE than in the neat BE (Table 1). This is because a CH₃(CH₂)₇ group of the OE that is one-bonded to one OH of a water molecule is more hindering to the approach of another OE molecule to the other OH of the water than the CH₃(CH₂)₃ group of BE. The A band of the water that is complexed with 3DN (Table 1) has essentially the same frequency as that in BE or OE, as expected. By contrast, the B and C bands of the water in the complex with 3DN are clearly different in frequency from those for BE or OE (Table 1), because the hydrogen-bonding strength of water to a carbonyl O atom is different from that of water to an ether O atom.

The vibrational mode ν_b of the “bonded” OH of a water molecule in the complex should sensitively depend on the strength of hydrogen bonding between the H atom of a water molecule and the O atom of a functional group. The absorption of ν_b should decrease in frequency as the strength of the hydrogen bond is stronger, resulting from the lengthening of the O—H bond of the water molecule.²⁶ The observed frequency of ν_b is 3509 cm⁻¹ for BE, while it is 3558 cm⁻¹ for 3DN, according to Table 1. This indicates that the strength of hydrogen bonding of water to an ether O atom is significantly stronger than that to a carbonyl O atom. It is suggested that the frequency of ν_b can be used to evaluate the strength of hydrogen bonding of water to a functional group.

The normal frequencies were calculated for the water that is hydrogen-bonded to one or two carrier molecules according to the procedure described in the above. In Table 2 the calculated frequencies are compared with the observed values of ν_f , ν_a , ν_s , and ν_b for the water that is hydrogen-bonded to the ether O atom of BE or 3DN in the one-bonded or two-bonded complexes. The calculated and observed frequencies are generally in good agreement with each other, to support the physical picture that the water dissolved in the solution or the liquid of the organic compounds is “one-bonded” or “two-bonded” to the functional groups depending on the surrounding environment. The varying absorptions of the water dissolved in the organic liquids including BE, OE, and 3DN were previously assigned to water—organic molecule clusters.^{12,13} Theoretically the “one-bonded” water was previously treated as a structure model for the hydrogen-bonded complex of water with organic molecules.²⁷ It is the first time, to our knowledge, that the structures of the “one-bonded” and “two-bonded” water have been definitely determined as the most basic interacting pattern of water with organic (or polymeric) materials on the basis of

TABLE 3: Solubility of Water in the BE Solution at Various Concentrations in *n*-Heptane at Room Temperature

composition of BE		solubility of water		molar ratio of water to BE
% (v/v)	mol/g ($\times 10^4$)	wt %	mol/g ($\times 10^6$)	H ₂ O/BE
0		0.0032	1.75	
5	3.34	0.0026	1.45	0.0043
10	6.76	0.0042	2.31	0.0034
25	17.2	0.017	9.21	0.0054
50	35.6	0.045	25.2	0.0071
75	55.4	0.080	44.1	0.0080
100	76.8	0.16	89.1	0.0116

the infrared spectra. The present study implies that the water dissolved in various polymers is mostly “two-bonded” from the infrared spectra, which show two clear absorptions in the 4000–3400 cm^{-1} region.^{14,15} This means that in most polymers the dissolved water is surrounded by sufficient functional groups to be fully hydrogen-bonded to in the interactive vicinity.

The solubility of water in the solution, representatively, of BE in *n*-heptane is given in Table 3, where the values are corrected for the partial solubility of water in *n*-heptane for its volume fraction at a concentration. The solubility of water increases with the increasing concentration of BE in the solution, as is expected from the spectra in Figure 2. The solubility is as small as 0.0026 wt % at the 5% (v/v) concentration of BE, and it increases to 0.16 wt % in the neat. The molar ratios of water to BE in the solution were calculated from the solubility, as given in the last column in the table. It is 0.0043 at 5% (v/v); that is, the population of the hydrated BE among all BE molecules is only less than 1 out of 200 at the concentration. The molar ratio gradually increases to 0.012 for the neat BE. It should be noted that all the hydrogen-bonded water is “one-bonded” to BE at the concentration 5% (v/v), while a part of the hydrogen-bonded water is “one-bonded” to BE and the other part is “two-bonded” in the neat, as is seen from the spectra in Figure 2. It is interesting how the population of the two species of the hydrogen-bonded water depends on the concentration of BE. However, it was not possible to quantitatively estimate the two populations, because the relative absorption coefficient of the 3692 and 3590 cm^{-1} bands, which are due to the “one-bonded” and “two-bonded” water, respectively, was not able to be experimentally determined.²⁸

Conclusion

In the present study we have developed the HIIR method as a new tool to study the interactions of water with organic compounds. This method was applied to the water in the solution of BE, OE, and 3DN in *n*-heptane. It was found that water is dissolved in an organic compound predominantly through hydrogen-bonding with a functional group possessed, while only a small fraction is dissolved by van der Waals interactions. The water is hydrogen-bonded to one functional group if this is isolated beyond the interactive vicinity from the other, while the water is hydrogen-bonded to two of them if two or more functional groups are within the interactive vicinity. The “one-bonded” or “two-bonded” water was definitely identified from the infrared absorptions.

The ratio of the hydrophobic portion against a functional group should be an important factor that affects the interactions of water with an organic compound. Another important factor that significantly influences the interactions is the property of the functional group. In the present study we treated with ether and carbonyl groups, the hydrogen-bonding power of which is

not so strong. The functional groups such as hydroxyl, amine, amide, and so forth should have stronger hydrogen-bonding power. The interactions with these functional groups should be studied to more generally understand the interactions of water with organic or polymeric materials.

The only limitation of the present method is that the hydrophobic medium must be liquid under the condition where the experiment is carried out. The experiment itself can be done very simply at room temperature or below or above this. A hydrophobic medium of saturated hydrocarbons is not special but may naturally occur. Thus, the HIIR method may be applied to study the interactions of water with various materials under nearly naturally occurring conditions.

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- (28) The intensity of the 3694 cm^{-1} band of the water, the molar absorptivity of which can be determined from the observed spectrum at the concentration 5% (v/v), where the water is essentially completely “one-bonded”, could be used to estimate the population of the species of the “one-bonded” water at a concentration, and then the population of the “two-bonded” water could be determined by subtraction of that from the solubility at the concentration. This was not, however, possible for the following reasons: First, the measured intensity at 5% (v/v), which is so weak, did not have sufficient accuracy for the estimation. Second, it was not possible to completely remove the contamination of humidity in air into the solution of P during the experimental procedure in the present experiment. The contamination seriously affects the reliability of the intensity of the weak absorption of the water dissolved, which is obtained by subtracting the spectrum of the P solution.