

NEAR-INFRARED SPECTROSCOPIC ANALYSIS FOR CLASSIFICATION OF WATER MOLECULES IN WOOD BY A THEORY OF WATER MIXTURES

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Abstract. This study was conducted to analyze the mechanism of moisture adsorption–desorption in wood using near-IR (NIR) spectroscopy. NIR spectra reflected from moist wood were acquired, and spectra in the range from 1800–2100 nm, which were sensitive to water variation, were decomposed into three different components according to the Buijs and Choppin theory. It is assumed that the three components represent three types of bound water: water molecules without -OH groups engaged in hydrogen bonds (S0), water molecules with one -OH group engaged in a hydrogen bond (S1), and water molecules with two -OH groups engaged in hydrogen bonds (S2). Ratios of the decomposed spectra of NIR absorbed by each type of water molecule were analyzed during changes in water adsorption–desorption states. Through this analysis, a sorption model for predicting the structural state of each water component in wood was constructed. This model may be used to explain the effect of each water component on the occurrence of hysteresis as well as the transient state between bound water and free water. Based on the model, it was concluded that the monomolecular water layer in yellow poplar wood formed below approximately 8% MC during adsorption. Additionally, the phenomenon of hysteresis was demonstrated by the difference between the ratios of the S2 components in desorption and adsorption.

Keywords: Water in wood, near-infrared spectroscopy, water mixture model, Buijs-Choppin theory.

INTRODUCTION

Moisture control is essential for the rational use of wood, which is a representative hygroscopic material. Moisture in wood is one of the most important factors that determines its physico-chemical properties, such as specific gravity, size, strength, and optical and electrical properties. To analyze and control these properties, many studies have been conducted on water in wood (Siau 1995; Jung et al 2008).

In general, water within wood is classified as free or bound. Free water is liquid-state water found in lumens or intercellular spaces. Because this water exists in wood just by capillary force and is not chemically associated with the cell wall, variations in free water have little effect on physical and chemical properties of wood. Conversely, water that is strongly associated with the cell wall in wood is classified as bound water. Bound water adsorbed by wood is held by intermolecular forces between water molecules and the major chemical components of wood, such as cellulose, hemicellulose, and lignin. The FSP occurs when the sorption sites in wood are fully filled with water molecules. Below the FSP, the physicochemical properties of wood vary significantly with changes in moisture content (Stamm 1964; Skaar 1988; Eom et al 2013). Many researchers have posited that the reactivity of hydroxyl groups in the cell wall and dipole interactions between water molecules play a significant role in the moisture

desorption/adsorption process. However, this hypothesis has not been clearly demonstrated at the molecular level because of a lack of appropriate analytical techniques.

In this study, near-IR (NIR) spectroscopy was used for interpreting the states of water in wood. The NIR absorption bands of pure water are known to appear at 960, 1063, 1450, and 1912 nm (Schwanninger et al 2011). We interpreted water states in the adsorption–desorption processes on the order of hydrogen bonding by analyzing the NIR absorption band, including the 1912-nm wavelength.

MATERIALS AND METHODS

Sample Preparation

Yellow poplar (*Liriodendron tulipifera*) was used in these experiments. The specimen was cut into a small rectangular plate with dimensions of 50 × 50 × 10 mm (radial, tangential, and longitudinal directions).

Isothermal Adsorption–Desorption Experiments

To analyze water states in the adsorption–desorption process, specimens were first dried in an oven. Using the schedule in Table 1, specimens were humidified at 12 different RH conditions in the adsorption process (0–100% RH) and

Table 1. Temperature and RH conditions used in the isothermal adsorption–desorption experiment.

Temperature (°C)	RH (%)											
25	0	15	30	40	50	60	70	80	90	95	99	100

in the desorption process (100-15% RH) until reaching equilibrium moisture content (EMC) for each except 100% RH. Because it is difficult to achieve 0% MC in a thermohygrostat, specimens were dried in a desiccator.

After completing the adsorption process, the thermohygrostat maintained 100% RH to supply supersaturated moist air for several hours. Supersaturated air has greater vapor pressure than saturated water vapor. We assumed that residual water vapors in the supersaturated air were transformed to liquid water droplets on the wood specimen surface. The desorption process was performed by reversing this procedure.

Acquisition of Near-IR Spectra

For measuring NIR spectra, an optical probe-type NIR spectrometer (NIR Quest 256-2.5; Ocean Optics, Dunedin, FL) was used in this study. The optical probe, connected to a tungsten–halogen lamp (20 W) light source, was composed of seven optical fibers. The outer six optical fibers illuminated the surface of the specimen with NIR rays, and the central optical fiber delivered the reflected rays to the spectrometer.

NIR reflectance spectra were acquired at the same position of the specimen when the specimen reached EMC during the adsorption–desorption processes. For decreasing variations in moisture content on the surface of the specimen caused by factors such as evaporation, NIR spectra were acquired in a thermohygrostat. To enhance the signal-to-noise ratio, 15 scans were averaged. NIR spectra were acquired at a spectral resolution of 6.3 nm.

Chemometric Analysis of Near-IR Spectra

In this study, we analyzed the states of water in wood using NIR spectra, monitoring variations in the water absorption band of wood. An NIR

spectrum, which is specially absorbed to or reflected from pure water, consists of four major absorption bands at 961, 1063, 1450, and 1912 nm (Maeda et al 1995). Similarly, water in wood also absorbs NIR spectrum around the four major absorption bands. To analyze the dependence of the state of water in wood on moisture content, NIR absorption spectra at each moisture content were decomposed. Although the spectrometer acquired NIR spectra from 1000 to 2400 nm, only the water absorption combination band from 1800 to 2100 nm was extracted for analysis.

Generally, in absorbance spectra, intensity means the amount of electromagnetic wave energy that was absorbed by water molecules. Each ratio of energy absorbed at the four major absorption bands by three different water components (S0, S1, and S2) is the same. However, in this study, the highest intensity absorption band among those bands was chosen and used for classifying the type of water components, because a high-intensity absorption band has more data and bigger variance than a low-intensity absorption band. Spectra in the range from 1800 to 2100 nm, which was the highest NIR absorbance intensity (Fig 1b), was decomposed for classifying the type of water components in this study.

To analyze the structure of water in wood, we had to choose a model of water structure because there has been controversy between two liquid water structure theories: the mixture and continuum models (Falk and Ford 1966). The continuum model describes liquid water as a complete water molecule network fully hydrogen-bonded with different hydrogen bond energies and geometries. This model explains that the average strength of hydrogen bonds in water is weaker than that in ice because of random distortion and elongation. In contrast, the mixture model describes liquid water as an equilibrium

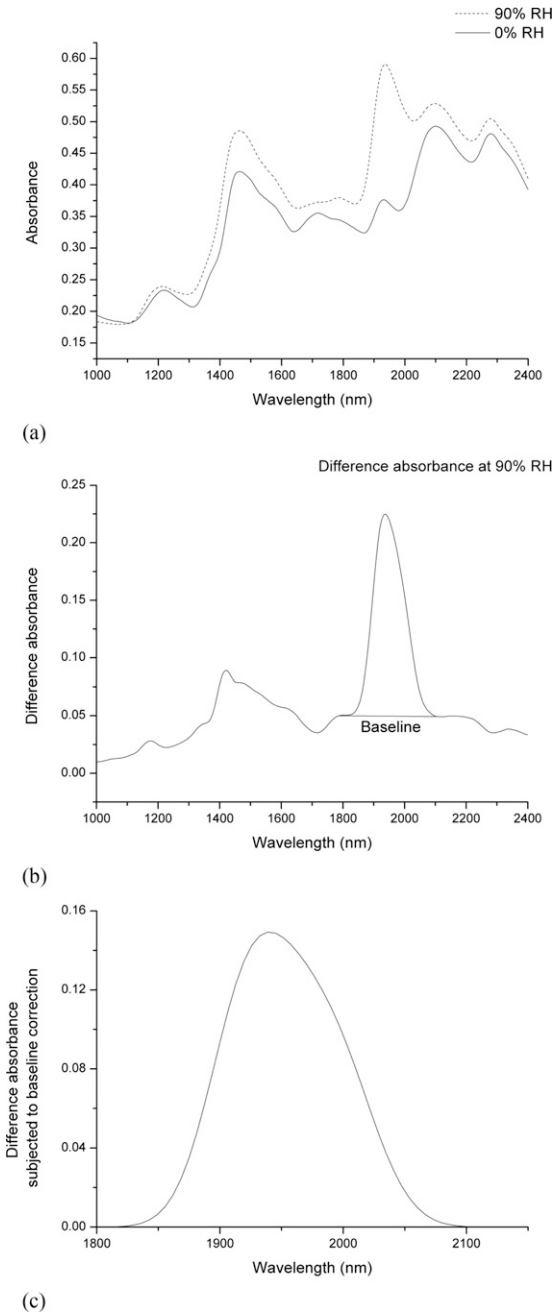


Figure 1. Procedures for calculating difference spectra (a) original spectra (RH = 90%, 0%), (b) difference absorbance spectra (subtraction from those for RH = 0%), (c) difference absorbance spectra after baseline correction.

mixture composed of different numbers of hydrogen bonds per molecule. This model explains that each water molecule has a different hydrogen bonding energy. Additionally, the proportion of each number of hydrogen bonds at particular temperature is maintained at an equilibrium state in this model. Although these two models still conflict with each other, we applied a water mixture model that is adjusted to the classical adsorption model of wood; this concept has been researched extensively in water structure analysis (Maeda et al 1995; Segnan et al 2001).

Buijs and Choppin (1963) proposed that water molecules could be classified into three categories: water molecules without hydrogen bonds (S0), water molecules with one -OH group engaged in a hydrogen bond (S1), and molecules with two -OH groups engaged in hydrogen bonds (S2). In fact, a water molecule is able to engage in four hydrogen bonds. However, because the hydrogen bonds involving the free orbitals of oxygen merely affect the vibrational energy of the water molecule, water molecules could be defined using just three categories. The theory of Buijs and Choppin has been researched consistently. Based on the theory, Perry and Li (1991), Tsuchikawa and Tsutsumi (1998), Tsai et al (2001), and Inagaki et al (2008) studied the effect of water bonding structures on interactions of water with solid substances.

In this study, difference absorbance spectra, which are the result of subtracting the NIR absorbance of each moisture specimen from that of the oven-dried specimen, were calculated to decompose the state of water molecules into three components (Fig 1a-b). This computation is able to decrease the overlap of NIR spectra with wood and simplify NIR absorbance spectra, causing them to only contain the variations of water molecules in wood. In the NIR region, there was a characteristic increase in absorbance as wavelength increased. Therefore, NIR spectra were baselined from 1800 to 2100 nm (Fig 1c). The difference spectrum subjected to baseline correction was expected to show only the variation of water equilibrated with atmospheric conditions.

RESULTS AND DISCUSSION

Categorizing Water Molecules by the Number of Hydrogen Bonds

One might be able to control the hydrogen bonding state of liquid water by thermal and chemical treatments (Fornés and Chaussidon 1978). However, it is difficult to precisely manipulate the state of water in wood artificially because wood has a complex structure. The NIR absorption band relevant to water in wood could be assigned statistically according to the number of hydrogen bonds formed by each water molecule. In this study, principal component analysis (PCA) was applied to assign bands by the number of hydrogen bonds involved. PCA, which is a type of multivariate analysis, has previously been used successfully to decompose the water sorption band (Tsuchikawa and Tsutsumi 1998; Inagaki et al 2008).

The water absorption band for each order of hydrogen bonding could be estimated from the spectral loading plot of principal component 2 (PC2) (Fig 2). The water absorption band from 1800 to 2100 nm was selected to separate the S0, S1, and S2 components. PCA was carried out on all baselined difference spectra, ranging from 0 to 99% RH (Fig 2).

A normal distribution with a center axis at 1951 nm was derived by principal component 1 (PC1), and it covers 98.59% of the variance of the raw

spectra. If we assume that water is composed of just one type of component, the peak at 1951 nm can represent that water component. However, because we assumed that water was composed of three types of components (S0, S1, and S2), three peaks should be derived by PC2. Thus, it is concluded that the three distinct peaks at 1868, 1930, and 2021 nm represent the three water components S0, S1, and S2, respectively, described by the Buijs-Choppin theory.

Although the baselined difference spectra are composed of the overlapped water absorption bands of each component, the absorption of each water component could be separated by a curve-fitting procedure using OriginPro 8 (Fig 3). If the absorbance of water molecules was assumed to be a normal distribution, the absorption of each water component could be expressed by an area-integrated method using Eq 1. In Eq 1, AI is area intensity, S_n is the name of the component delineated by the order of hydrogen bonding ($n = 0, 1, \text{ or } 2$), and $DA(\lambda)$ is the baselined difference absorbance at wavelength λ .

$$AI(S_n) = \int DA(\lambda) d\lambda \quad (1)$$

Variation of Water in Wood Observed by Spectral Decomposition

Bound water in wood is known to be associated with the cell wall or with other bound water.

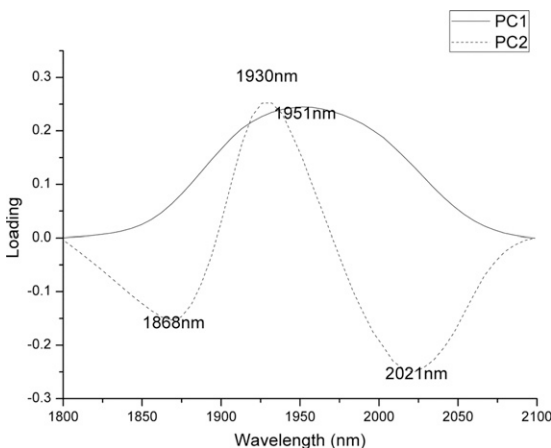


Figure 2. Loading plots of the first and second principal components (PC1 and PC2) for the specimen.

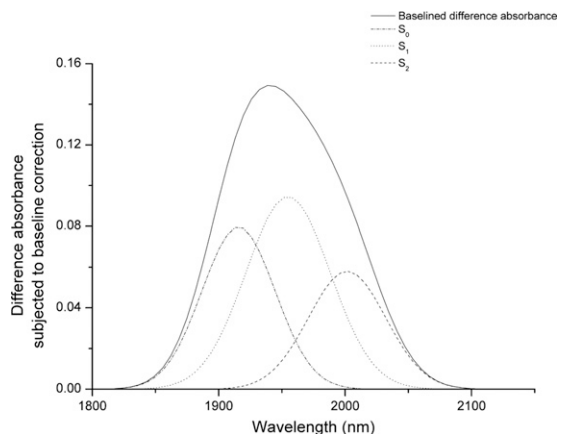


Figure 3. Baselined difference absorbance and decomposed spectra of the specimen.

Wood contains sorption sites, which comprise the -OH and -COOH groups in cellulose, hemicellulose, and lignin. In particular, the association of water molecules with the cell wall primarily occurs at -OH groups because the -OH group is the most abundant functional group.

In the early stage of water adsorption by oven-dried wood, water vapor molecules in the air first become hydrogen-bonded with sorption sites of the cell wall. The first absorbed water molecules are called monomolecularly absorbed water. As the adsorption process continues, water molecules in the surrounding air continue to form hydrogen bonds with the absorbed water until EMC is reached. The water molecules lay-

ered on monomolecularly absorbed water are called polymolecularly absorbed water (Skaar 1988; Hartley et al 1992). The absorbed water layers in wood are shown in Fig 4.

With respect to bound water in wood, each adsorbed water molecule is hydrogen-bonded. Using the concept of liquid water molecule components (S0, S1, and S2) of the Buijs and Choppin theory, we separated the states of water in wood. We supposed that the state of water depends on the order of hydrogen bonding. In our model, the oxygen atom of the water molecule is hydrogen-bonded to the hydrogen atom of an -OH group at a sorption site of wood, and the same mechanism is assumed to take place in polymolecular layer expansion.

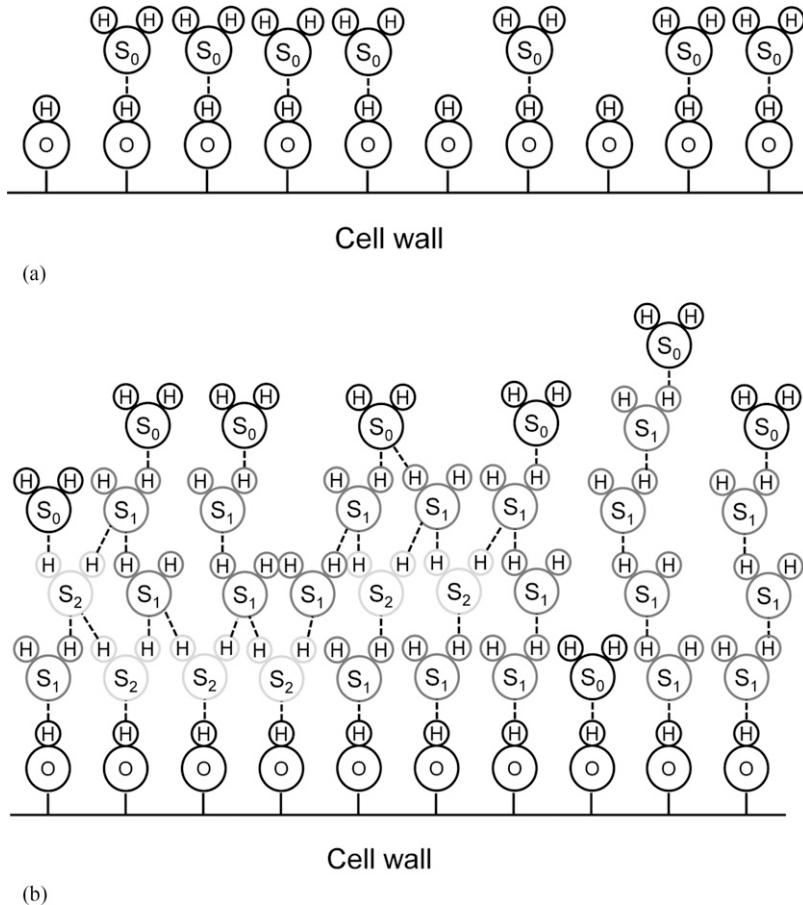


Figure 4. Bound water molecules hydrogen-bonded to sorption sites (a) initial stage of adsorption, (b) later stage of adsorption.

Figure 4 shows bound water molecules hydrogen-bonded to sorption sites. In Fig 4, large and small circles express oxygen and hydrogen atoms, respectively. Dotted lines represent the hydrogen bonds. The S_n in large circles expresses the state of the water molecule itself depending on the Buijs and Chopin theory. The n of S_n means number of hydrogen atoms of one water molecule bonded to the oxygen atom in the adjacent water molecule.

Figure 4a shows the initial adsorption stage. In this stage, top water molecules are determined as the S_0 component. As the adsorption process goes on, water vapor in the air is stacked on the top water molecules in the adsorption layer. When the former top water molecule (S_0) is put between the new top water molecule and the sorption site, the former water is converted to the S_1 component.

Figure 4b is a schematic molecular model for expressing late-stage adsorption. As polymolecularly adsorbed waters grow, the probability of hydrogen bonding with adjacent water molecules increases. In this case, S_0 components attached to sorption sites are converted to S_1 and/or S_2 components by hydrogen bonding with near water molecules. That is, S_2 components are abundant at high EMC.

The S_0 component, water without -OH groups engaged in hydrogen bonds (equivalently, water with no hydrogen bond at either of its own hydrogen atoms), can exist as monomolecularly adsorbed water or as the water molecule located at the top of the polymolecularly adsorbed water layer (Tsuchikawa and Tsutsumi 1998).

The S_1 component, which consists of water molecules with one -OH group engaged in a hydrogen bond (equivalently, water with a hydrogen bond at one of its own hydrogen sites), can exist as an adsorbed water molecule in the polymolecular layer between the sorption site and the top monomolecular layer water molecule. In the adsorption process, the polymolecular layer increases with moisture content of wood. In this case, the oxygen atom of a water molecule in water vapor attaches to the hydro-

gen atom of monomolecular water in a progressive process. As a result, the top water molecule in the adsorbed layer is converted from an S_0 component to an S_1 component.

The S_2 component, which consists of water molecules with two -OH groups engaged in hydrogen bonds (equivalently, water with a hydrogen bond at each of its own hydrogen sites), can exist as an adsorbed water molecule with extra hydrogen bonds in the polymolecular layer. The S_2 component could appear at high moisture content because when the adsorption layer grows, water molecules become closer, and more opportunities to bond with other water molecules occur in the three-dimensional structure of the adsorption layer.

S2 Component

When analyzing the moisture adsorption-desorption process in wood, it was more effective to understand the change in the water state of wood if the S_2 component was analyzed first. As shown in Fig 5a, in the adsorption process, the AI of the S_2 component was nearly zero until reaching 70% RH (9.54% MC). From 70 to 90% RH (16.4% MC), there was a rapid increase in the S_2 component. Then, the AI of S_2 showed similar values between 90 and 99% RH (21.75% MC).

The rapid increase in the S_2 component after reaching 9.54% MC during the adsorption process could be explained by the idea that adsorbed water in the polymolecular layer started to engage in additional hydrogen bonding with nearby water molecules in the layer. This effect means that there is a threshold for extra bonding. When they overcame the threshold, the water molecules rapidly interacted as moisture content increased. However, between 90 and 99% RH, there was no significant change in the S_2 component. This result means that most hydrogen bonding between neighboring adsorbed water molecules is complete at approximately 16.4% MC.

In the desorption process, AI of the S_2 component decreased rapidly from 95% RH (20.91%

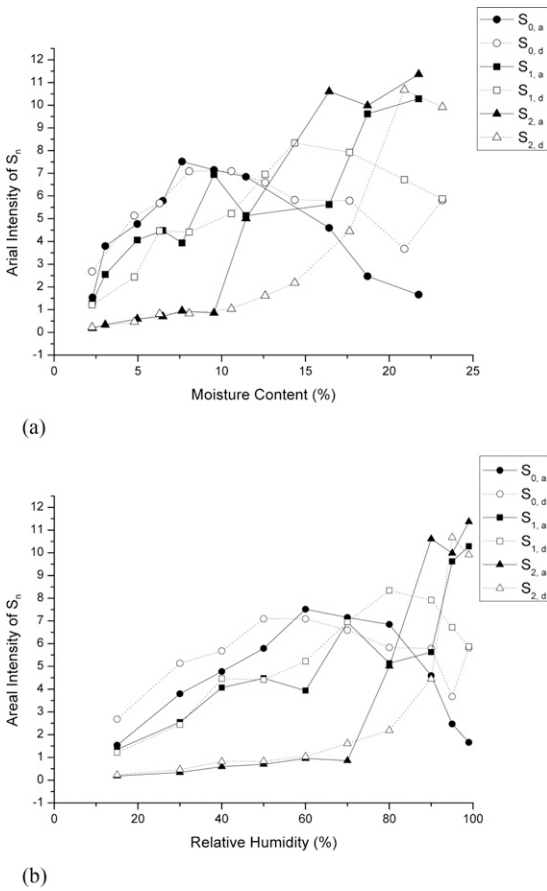


Figure 5. Areal intensities of S0, S1, and S2 components during adsorption and desorption (a) water components vs moisture content (MC), (b) water components vs RH (subscript a means adsorption process, subscript d means desorption process).

MC) to 60% RH (10.57% MC). Between 60% RH and the oven-dried state, AI of S2 in desorption was similar to that in the adsorption process. The reason for the S2 component decrease was concluded to be that evaporation of one S2 water molecule caused the conversion of two S2 water molecules to the S1 component. Because hydrogen bonding energy decreases as the order of hydrogen bonding increases, the evaporation of S2 water is easier and faster than that of the other types of water, S0 or S1. When one fully hydrogen-bonded S2 water molecule evaporates, hydrogen bonding between the oxygen atom of the evaporated water molecule and a hydrogen atom of a nearby S2 water molecule,

which was bonded to the evaporated water molecule, is broken.

We posited that this difference in S2 AI between adsorption and desorption could be a cause of hysteresis. The range of variation of the S2 component in the adsorption process (70-90% RH) is smaller than that in the desorption process (95-60% RH).

At high RH, >60%, capillary condensation can become an important factor and is responsible for the EMC–RH tailing upward.

The existence of capillary condensation could be proven by the rapid increase and decrease of the S2 component during adsorption and desorption, respectively, at high RH (Fig 5b) because S2 has a shape that is more appropriate for bonding each other compared with S0.

S1 Component

In the adsorption process, the AI of the S1 component consistently increased with an increase in moisture content. This result could be explained by the amount of increase of polymolecularly adsorbed water. In particular, the AI of S1 increased rapidly between 90 and 99% RH (21.75% MC). In this range, the polymolecularly adsorbed layer might form additional hydrogen bonds with another adsorbed layer that has grown on another cell wall. Because top-layer water molecules, which are S0 components, bond with other top-layer mono water molecules grown on other cell walls in the high RH condition, top-layer S0 water molecules are converted to S1 components.

In the desorption process, the AI of the S1 component increased as RH decreased from 99 to 80% RH (14.36% MC). This can be interpreted as a state-change relationship between the S2 component and the S1 component. As S2 water evaporated with the breakage of hydrogen bonds, the other S2 components remaining in the adsorption layer were converted to S1 components. As the desorption process continued, the S1 component consistently decreased with RH decrease from 80 to 15% RH (2.27% MC).

This effect was caused by the decrease in the polymolecular layer.

S0 Component

In the adsorption process, the AI of S0 increased until reaching 60% RH (7.63% MC). This might be the result of sorption sites in the cell wall being fully occupied with water molecules. As previously mentioned, monomolecularly adsorbed water and top-layer mono water molecules were S0 components in our model. In this range, the polymolecular layer (S1 component) and the S0 component grew with moisture content. Considering the change in the S1 component in this range, it could be concluded that the polymolecular layer growth started before the monomolecular adsorption was completely finished. This phenomenon occurred because of steric hindrance and accessibility. From 60 to 99% RH, the AI of S0 decreased at the end of the adsorption process. In this range, it was supposed that polymolecularly adsorbed water was converted to the S1 or S2 component, binding to nearby water molecules. At 99% RH, the top mono water molecule in the polymolecular layer was converted to an S1 component by binding to other mono water molecules grown on another cell wall.

In the desorption process, the S0 component showed a high AI at 99% RH (23.17% MC). This might be because of the occurrence of capillary water above FSP. However, this explanation is just a hypothesis, which should be further researched. The change in the S0 component proceeded as the reverse of the adsorption process. The increase in the S0 component during desorption from 99 to 50% RH (8.06% MC) resulted from the rebound of the decrease in the S2 component. In other words, when water molecules with many hydrogen bonds (ie the S2 component) evaporated, the S0 component was created. As desorption proceeded from 50% RH to the oven-dried state, the AI of S0 decreased. The reason for the decrease of the S0 component in this range could be concluded to be evaporation of monomolecularly adsorbed water from sorption sites. During the adsorption and desorp-

tion processes, the maximum AI of S0 appeared at approximately 8% MC. Monomolecular water adsorption on sorption sites would be complete at approximately 8% MC.

CONCLUSIONS

Using PCA of NIR spectra of water adsorbed to moist wood, we succeeded in extracting three different types of bound water molecule components (S0, S1, and S2), which are distinguished by the number of hydrogen bonds formed by the hydrogen atom of the water molecule. It was found that the change of ratios of each water component during adsorption was different from that in desorption.

The ratios of the three types of water molecule components in wood during adsorption and desorption were analyzed quantitatively, and we established a sorption model to explain the creation and dissolution of each water component.

With our model, we found that monomolecular water adsorption on sorption sites would be completed at approximately 8% MC. Additionally, we found that there was a large difference between S2 components in adsorption and in desorption; thus, among the three types of water, the S2 component played the major role in causing hysteresis.

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