Studies on Absorbed Water in Cellulose by Broad-Line NMR

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Synopsis

Nuclear magnetic resonance absorption spectra of linter cellulose containing various amounts of water were studied to clarify the relation between the amount of absorbed water in cellulose fiber and the molecular motion in such a cellulose–water system. An amorphous cellulose sample was used for the sake of comparison. The changes in line width and second moment of the spectra were measured at various temperatures. From the variation with temperature of the first-derivative curves and the second moments, it has been inferred that the proton movement of absorbed water changes markedly over the approximate range 180°–200°K and that the absorbed water lowers the glass transition temperature of cellulose to room temperature.

INTRODUCTION

There are a number of studies on the effect of absorbed water in cellulose. The molecular motion in such a cellulose–water system has not, however, been fully clarified. Water may be held by cellulose fibers in a number of ways. In the interaction between absorbed water and cellulose, the activity of the water increased in the following order[1]: (a) water hydrogen-bonded to the free hydroxyl groups in the noncrystalline regions of cellulose, (b) multilayer water, (c) capillary water, and (d) bulk water.

For the investigation of molecular motion in cellulose, it is helpful to consider the intermolecular distances in the noncrystalline regions. These intermolecular distances are roughly divided into two main groups of comparatively broad (the A region) or narrow (the B region) distances.[2] The range comprising the A and B regions is from several hundred angstroms down to, presumably, the size of water molecules. As the amount of water increases from zero, it will be absorbed first in the A region (bonding water A), and on further increase it will be absorbed with the cleavage of intermolecular hydrogen bonds in the B region (bonding water B). From these considerations, it is expected that bonding water A makes little contribution to molecular motion, but bonding water B greatly diminishes intermolecular forces and decreases the glass transition temperature T_g.

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The aims of this paper are to further clarify (a) how absorbed water influences molecular motion in cellulose, and (b) how the behavior of the absorbed water changes with temperature.

EXPERIMENTAL

Samples

The following samples (except no. 2) were extracted with an alcohol: benzene (1:2) solution.

Sample no. 1: Linter cellulose dried at 418°K under 10^{-4} mm Hg for 3 hr. This sample is expected to be absolutely dry.[3,4] It is not possible to dry such a sample absolutely in the usual drying conditions at 378°–383°K.

Sample no. 2: Amorphous cellulose dried at room temperature under 10^{-4} mm Hg for about 70 hr. This sample was prepared by treating cellulose triacetate sheets with 1% sodium ethylate dissolved in anhydrous ethanol. The saponification was allowed to proceed at room temperature for two days. This sample was also expected to be absolutely dry, and a DSC curve showed no endothermic peak from absorbed water.

Sample no. 3: Linter cellulose dried at room temperature under 10^{-4} mm Hg for 3 hr. This sample contains very small amounts of water (about 0.5% w/w).

Sample no. 4: Air-dried linter cellulose containing 4.6% water.

Sample no. 5: Linter cellulose containing 24.2% water.

Sample no. 6: Linter cellulose containing 47.0% water.

The above samples were sealed in glass tubes 10 mm in diameter and about 200 mm in length.

Apparatus

The NMR apparatus used was a Japan Electron Optics Laboratory, JNM-W-40 type nuclear magnetic resonance spectrometer. The temperature of the samples was controlled by a JES-UCT-2 type variable temperature adapter. By the use of the adapter, the sample temperature could be maintained within a range of less than ±0.1°K at temperatures between 100° and 430°K. The sample temperature was measured by means of a thermocouple in contact with one end of the sample.

RESULTS

Line Shapes and Line Width Changes

Figures 1 and 2 cover the lower half of the range of the applied magnetic field and show the first-derivative curve for linter cellulose at various temperatures. In Figure 1, the absorption at 313° and 315°K contains broad (rigid state) and narrow (proton motion) components. Here, the samples being observed are the absolutely dried linter cellulose (no. 1) and the linter cellulose containing very small amounts of water (no. 3). The ab-
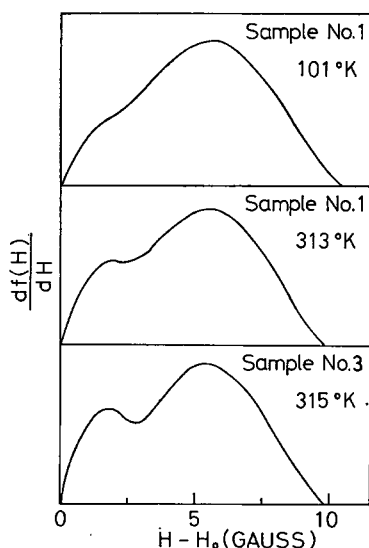
Fig. 1. First derivative curve of the proton resonance as a function of the applied magnetic field for samples no. 1 and no. 3.
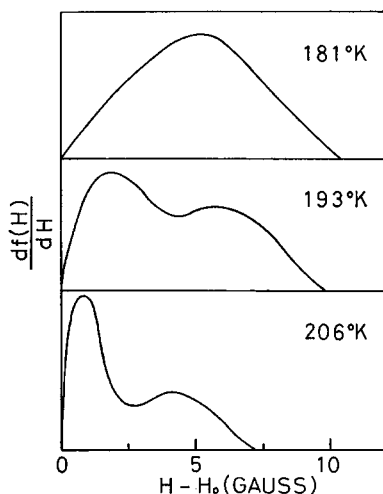

Fig. 2. First derivative curve of the proton resonance as a function of the applied magnetic field for sample no. 5.

sorption of sample no. 1 at 101°K also contains broad and narrow components although the narrow component is only a vague shoulder. In Figure 2, for linter cellulose containing large amounts of absorbed water (no. 5), the proton movement can be seen to change markedly around 190°K.

Figures 3, 4, and 5 show the variation of the line width with temperature for absolutely dried linter cellulose, dry amorphous cellulose, and linter cellulose containing 24.2% water, in that order. The line width was taken
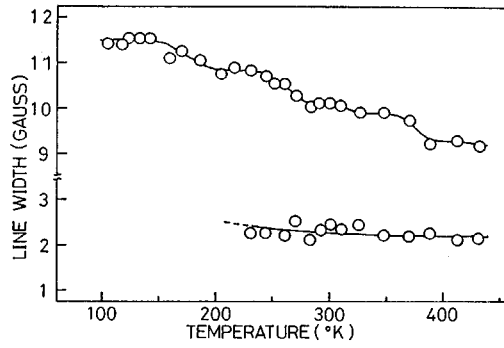
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Fig. 3. Variation of line width with temperature for sample no. 1, linter cellulose dried at 418°K under 10^{-4} mm Hg for 3 hr.
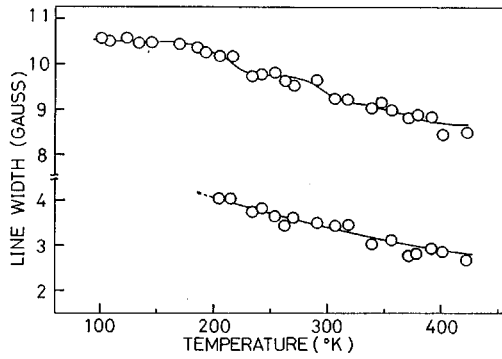

Fig. 4. Variation of line width with temperature for sample no. 2, amorphous cellulose dried at room temperature under 10^{-4} mm Hg for about 70 hr.
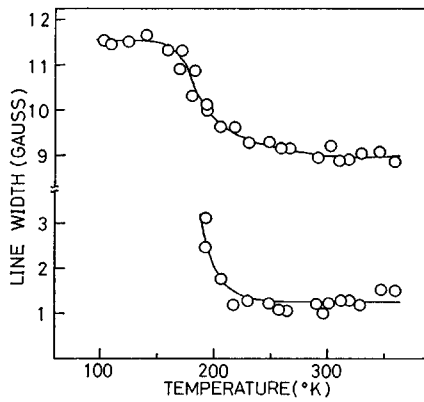

Fig. 5. Variation of line width with temperature for sample no. 5, linter cellulose containing 24.2% water.

as the separation, in gauss units, between corresponding maxima and minima of the first derivative of the absorption with respect to the applied magnetic field.

For absolutely dried linter cellulose, the width of the broad component was 11.4 gauss at 110°K, and with increasing temperature (at around 150°K) it showed a tendency to decrease. Below 200°K, the narrow component appeared as only a shoulder, and because of the poor resolution of the broad component, the width shown for the broad component is the total width. The width of the narrow component above 200°K was approximately constant, 2.5–2.3 gauss, as the maximum temperature, 430°K, was approached.

For the amorphous cellulose, the width of the broad component showed similar tendencies. It was 10.5 gauss at 101°K, and decreased with increasing temperature, reaching 8.5 gauss at 430°K. Below 200°K, the narrow component appeared as a shoulder, and above this temperature its width decreased gradually to 2.8 gauss at around 400°K.

For the linter cellulose containing 24.2% water, the width of the broad component was 11.5 gauss at 100°–150°K. At 150°K, it decreased rapidly to 9.2 gauss and remained approximately constant to 360°K. The narrow component appeared above 190°K (see Fig. 2) and decreased rapidly to a width of 1.1 gauss, remaining approximately constant to 340°K.

Change in the Second Moment

Figures 6 to 11 show the variation of the second moment of the line width with temperature for each sample. For absolutely dried linter cellulose (Fig. 6), the second moment decreased in a stepwise manner. The second moment was 14.0 gauss^2 at 101°K. It dropped to 12.8 gauss^2 to 210°K. Above this temperature, it dropped again to 11.6 gauss^2, then remained approximately constant to 290°K, then dropped again to 10.1 gauss^2, after which it remained approximately constant up to 430°K.

For the amorphous cellulose (Fig. 7), the second moment was 12.5 gauss^2 at 101°K and decreased continuously to 11.3 gauss^2 at 180°K, then re-
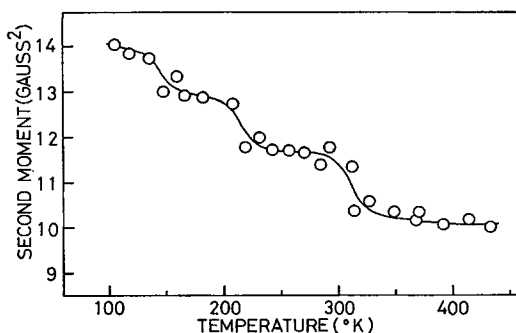

Fig. 6. Variation of the second moment of the absorption line with temperature for sample no. 1, linter cellulose dried at 418°K under 10^{-4} mm Hg for 3 hr.
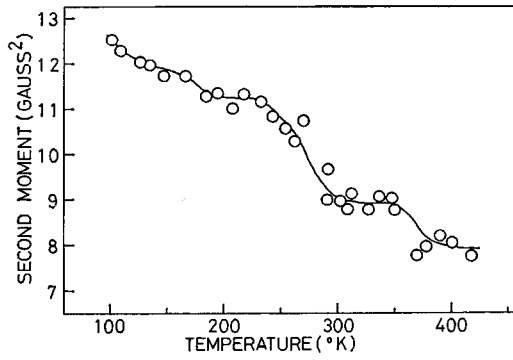
Fig. 7. Variation of the second moment of the absorption line with temperature for sample no. 2, amorphous cellulose dried at room temperature for about 70 hr.
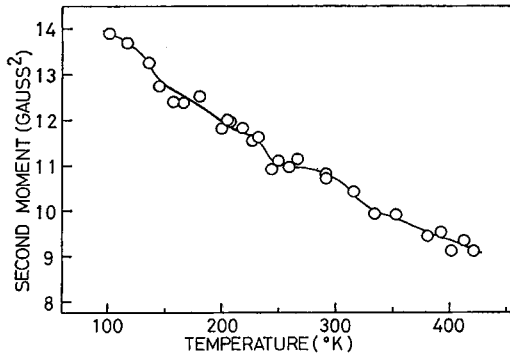

Fig. 8. Variation of the second moment of the absorption line with temperature for sample no. 3, linter cellulose dried at room temperature under 10^{-4} mm Hg for 3 hr.
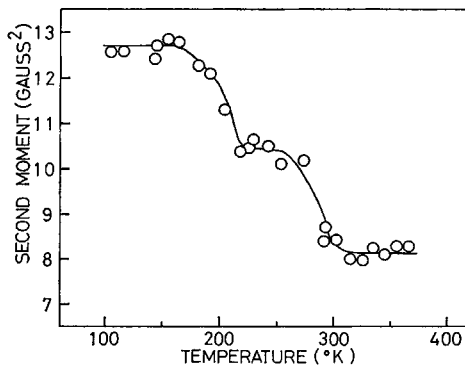

Fig. 9. Variation of the second moment of the absorption line with temperature for sample no. 4, air-dried linter cellulose containing 4.6% water.
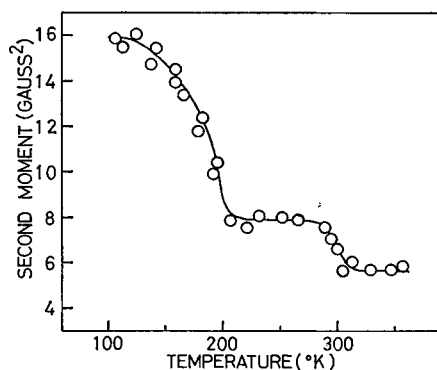
Fig. 10. Variation of the second moment of the absorption line with temperature for sample no. 5, linter cellulose containing 24.2% water.
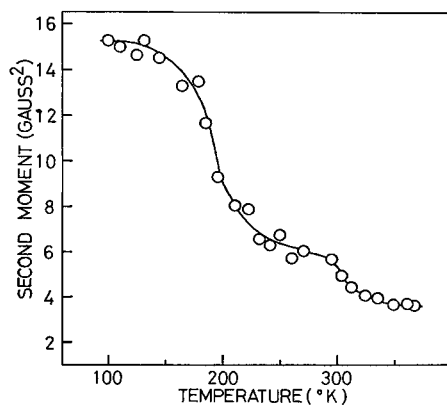

Fig. 11. Variation of the second moment of the absorption line with temperature for sample no. 6, linter cellulose containing 47.0% water.

mained constant up to 230°K. Above this temperature, it decreased rapidly to 9.0 gauss², and then stayed constant up to 360°K. Above 360°K, it dropped to a final value of about 7.7 gauss².

For the linter cellulose dried at room temperature under 10^{-4} mm Hg (Fig. 8), the second moment was 13.8 gauss² at 101°K and decreased rather continuously to 11.5 gauss² at around 230°K. At this temperature, it dropped to 10.9 gauss² and remained constant up to 290°K, after which it decreased gradually to a final value of 9.0 gauss².

The curves for the high water-content samples, including the air-dried sample, were markedly different from those for the above samples. For air-dried linter cellulose (Fig. 9), the second moment was 12.7 gauss² at 105°K and remained constant up to 170°K. It decreased rapidly above this temperature to 10.5 gauss² at 220°K and remained constant up to 270°K, then decreased rapidly again over the range 270°–290°K.

For the linter cellulose containing 24.2% water (Fig. 10), the curve was similar to the curve for the air-dried sample. It contained two sharp de-

creases, one over $150°–210°K$ and the other around room temperature, $270°–300°K$.

For the linter cellulose containing 47.0% water (Fig. 11), the curve was very similar to the 24.2% water and air-dried cases.

DISCUSSION

The first-derivative curves shown in Figures 1 and 2 are interesting. In the case of the absolutely dried linter cellulose the narrow component is first observed around $101°K$. This indicates that some local molecular motion exists in the amorphous region, even though it is not distinctly visible at such low temperatures (Figs. 3 and 4) and even though the molecular main chains in the amorphous region are generally rigid at such temperatures. In the case of the linter cellulose containing much water (24.2%), however, the narrow component is not observed even at $181°K$. It seems that molecular motion is restricted below this temperature by the strong hydrogen bonding of the absorbed water. Another possible factor is that a magnetic dipolar broadened resonance will usually start to narrow when the atomic conformation about the nuclei being observed changes significantly within a time interval defined by the frequency width of the broadened line. Based on these considerations, it becomes clear why the proton movement changed markedly over the approximate range $180°–200°K$, as shown in Figures 2 and 5. That is, molecular motion of the absorbed water became active above this temperature range. This will be further discussed later.

Information concerning molecular motion can also be obtained from the curves of second moment versus temperature. It is possible to calculate the second moment of the absorption line from the known molecular structure,[5] and a comparison can be made between experimental values and the calculated ones.

The second moment, $\Delta H_2{}^2$, is defined as

$$\Delta H_2{}^2 = \int\! f(H)(H - H_0)^2 dH / \int\! f(H) dH$$

$$= {}^1/_3 \int\! f'(H)(H - H_0)^3 dH / \int\! f'(H)(H - H_0) dH$$

where H is the value of the applied magnetic field.

The rigid-lattice second moment of the methylene group[5] is 18.2 gauss^2; that of the methine group,[6] about 3 gauss^2; and that of the hydroxyl group,[7] 12.4 gauss^2.

The rigid-structure second moment for cellulose was estimated as 8.9 gauss^2 by the method of Gutowsky and Pake.[5] The experimental second moments of linter cellulose and amorphous cellulose were 14.0 and 12.5 gauss^2, respectively. The second moment can be divided into intra- and intermolecular contributions,

$$\Delta H_2{}^2 = (\Delta H_2{}^2)_{\text{intra}} + (\Delta H_2{}^2)_{\text{inter}}.$$

As the second moment calculated by the method of Gutowsky and Pake is the intramolecular component, the difference between the calculated value and the experimental value can be attributed to the intermolecular component, caused by intermolecular interactions such as structure strain from hydrogen bonding. The difference of 1.5 gauss^2 between amorphous and linter cellulose can be assigned to crystalline contributions from linter cellulose.

For the absolutely dried linter cellulose (Fig. 6), the second moment is discontinuous at 140°, 210°, and 300°K. To fully clarify the transition phenomena occurring at 140° and 210°K, further experiments with model compounds are required. The decrease in the second moment around 300°K is observed from dilatometric measurements,[8] broad-line NMR,[9] and dielectric measurements[10] and is caused by the cleavage of weak hydrogen bonds in the amorphous region.

A similar mechanism is expected in amorphous cellulose (Fig. 7). However, a somewhat larger decrease in the second moment, shifted to below 300°K, was observed. This shift is due to amorphous cellulose containing little or no crystalline structure, hence the average intermolecular distances are greater.

Such transitions for simple compounds have been investigated semi-quantitatively by broad-line NMR.[9,11] The complexity of the hydrogen bonding in cellulose makes such investigations difficult.

For the linter cellulose dried at room temperature under 10^{-4} mm Hg, the second moment decreased nearly continuously over the temperature range 110°–420°K (Fig. 8). This is attributed to the presence of a small amount of water. A small amount of water would be distributed randomly by monolayer absorption in the A region.

The high water-content samples showed two rather large discontinuities, one occurring over the range of about 180°–220°K and the other around room temperature, 270°–300°K (Figs. 9, 10, and 11). For the drop in second moment occurring near room temperature, the magnitude of the decrease becomes smaller as the water content increases. This narrowing is caused by increasing movements of cellulose protons. As is known, the elastic modulus of cellophane decreases sharply above 6% water content,[12] and T_g for cellophane containing more than 6% water decreases to room temperature. Wada[2] concluded that a water content of 6% marked the boundary between bonding water A and bonding water B in cellophane. It is probable that the proton movement in the high water-content cellulose at around room temperature results from the occurrence of the glass transition. Thus, it can be concluded that several per cent of water absorbed by cellulose break the hydrogen bonds in the B region, also causing a decrease in T_g, as supposed by Wada for cellophane. Furthermore, the decrease in the second moment at this temperature corresponds to the transition temperature for water-swollen cellulose, T_w, reported by Lamiah and Goring.[8]

The decrease in the second moment over 180°–220°K corresponds to the temperature range in which a narrow component in the first-derivative
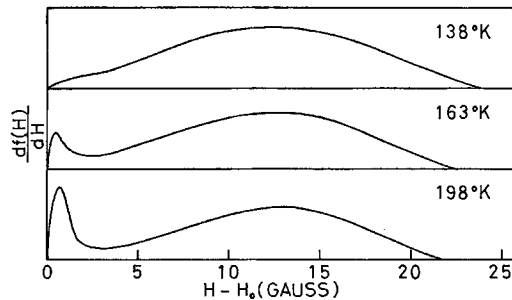
Fig. 12. First derivative curve of the proton resonance as a function of the applied magnetic field for distilled water.
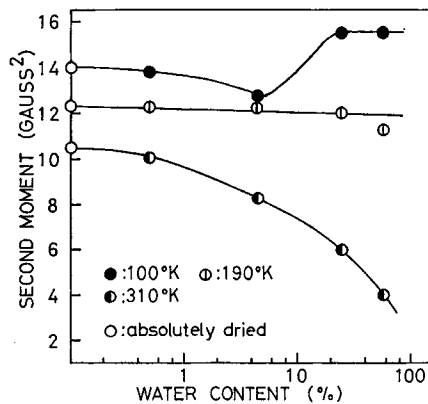

Fig. 13. Second moment vs. water content curve for linter cellulose.

curves becomes prominent (Figs. 2 and 5).   This indicates that the absorbed water in the cellulose fiber becomes active in and above this temperature range.   As the proton movement measured by broad-line NMR does not always indicate large-scale molecular motion, "active state" must be distinguished from "nonfrozen state."   There is a good deal of proton motion even below the freezing point, as shown for pure water in Figure 12.

Although the narrow component cannot be seen below 180°K in the high water-content sample (Fig. 2), it can be seen at temperatures as low as 163°K in pure water (Fig. 12), and some of the absorbed water in the high water-content samples certainly exists as bulk water.   From this it may be concluded that such bulk water is influenced by the cellulose fibers in a way which restricts the motion of the water protons,[13] and, as a result, the relaxation times become longer[2] as compared with free water.

The second moment of linter cellulose versus water content for the five samples at different temperatures is plotted in Figure 13.   At 100°K, the second moments of the high water-content samples, (no. 5 and 6), which contain bulk water, are higher than that of the absolutely dried linter cellulose, but the second moments of the two intermediate samples, no. 3 and 4,

are lower. Two reasons are supposed for these lower values. One is the decrease in structure strain due to the cleavage of hydrogen bonds. The other is the formation of multilayer or of capillary water, which is different from bulk water.

The existence of water is apparently an insignificant factor at 190°K. The value of the second moment is approximately constant, 12 gauss^2, for all water contents. At this temperature, the protons of water have almost the same activity as those of cellulose. The narrow component from water in the first-derivative curves will temporarily disappear at this temperature.

Above 200°K, as the water content becomes higher, the second moment becomes lower, as shown at 310°K in Figure 13.

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