

Temperature Dependency of Bound Water of Cellulose Studied by a High-Resolution NMR Spectrometer

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Synopsis

The widths at half-value of high-resolution NMR spectra of bound water of cellulose were studied in relation to the temperature change. Two points were made clear: First, the amount of bound water of the cellulose sample can be pointed out with higher accuracy the lower the temperature of the measurement. Second, it is possible to determine in a simple manner the boundary temperature T_c at which water molecules become bound by the cellulose. T_c is characteristic of the cellulose sample of a given water content and corresponds to the glass transition temperature of the water-containing sample. The measurements appear to be readily applicable to other hydrophilic polymers.

INTRODUCTION

The preceding study on the width at half-value of high-resolution NMR spectra¹ indicated that water in cellulose fibers is present in two distinctly different states of binding and the content of the strongly bound water (to be defined as bound water) is influenced greatly by the kind and state of cellulose fibers, varying in the range of 15% to 25% for the samples under study. When measurements are made by changing the temperature of samples, however, the presence of a low temperature region showing strong differential energy of water binding is observed below a certain temperature which is characteristic of each sample, and this observation shows that the state of bound water in the samples is also influenced to a considerable extent by a change in temperature.

The present study was undertaken with a view to examining the state of bound water in relation to temperature change and looking into the relationship between cellulose and water in detail.

EXPERIMENTAL

Commercial softwoods dissolving pulp (DP), hardwoods semichemical pulp (SCP), and absorbent cotton (cotton) were used as cellulose samples.

The beaten pulps and the samples hydrolyzed with hydrochloric acid as well as swollen by sodium hydroxide were prepared by the method described in the previous paper.¹ The resultant moist samples were dehydrated to given water contents, each was packed in a sample tube, and the high-resolution NMR absorption spectrum was measured. A Japan Electron Optics Laboratory NMR spectrometer Model TNM-C-60HL with its accessories for varying temperature was used under the following conditions; resonance frequency, 60 Mc; sweep rate, 90 ppm/2.5 min; RF level, 40 db; sample temperature, varied from -30°C to 95°C .

RESULTS AND DISCUSSION

The relationships between the width at half-value and the water content determined on the unbeaten DP samples at several temperatures are shown in Figure 1. It is apparent from this figure that the range of the low water content region showing strong differential energy of water binding is nearly independent of the measuring temperature, and a change in the width at half-value tends to become steeper as the measuring temperature falls. This proves that the lower the measuring temperature, the more accurately the amount of bound water can be pointed out. In the high water content region, changes in the width at half-value remain extremely small in the temperature range of -20°C to 40°C , but tend to increase rapidly below -20°C .

The relationships between the width at half-value and the water content are shown for beaten DP and cotton in Figures 2 and 3, respectively. The same relationship as seen for the unbeaten DP holds for each of these

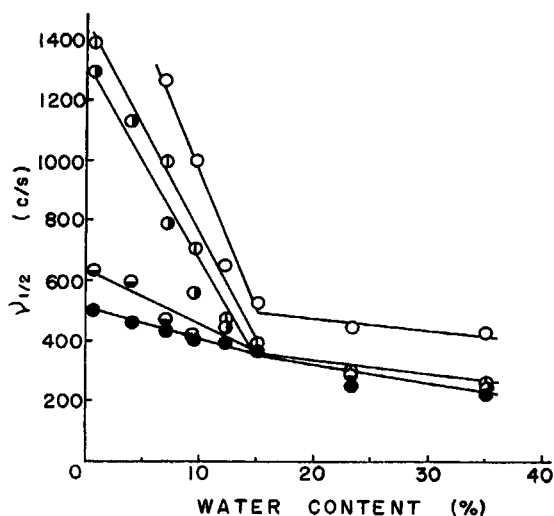


Fig. 1. Relationship between width at half-value and water content in unbeaten DP sample at various temperatures: (●) 40°C ; (◐) 24°C ; (◑) 0°C ; (◒) -20°C ; (○) -30°C .

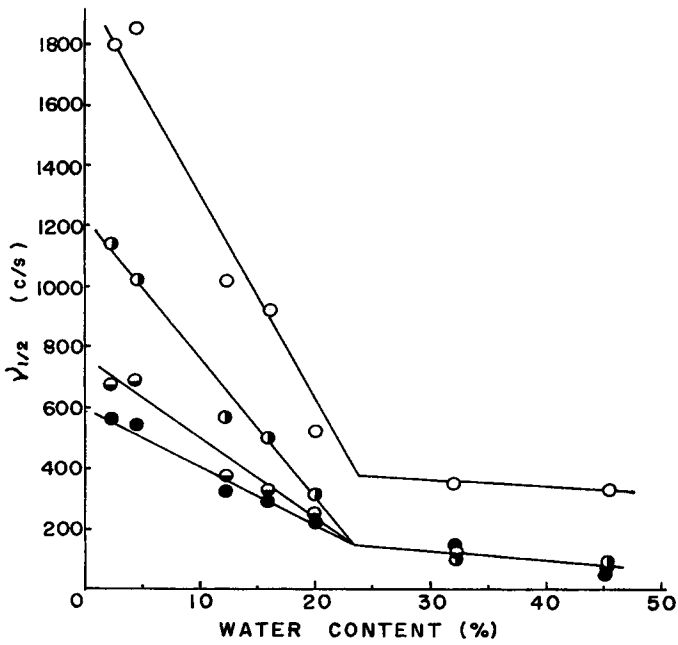


Fig. 2. Relationship between width at half-value and water content in beaten DP sample (64°SR) at various temperatures: (●) 40°C; (◐) 24°C; (○) 0°C; (○) -30°C.

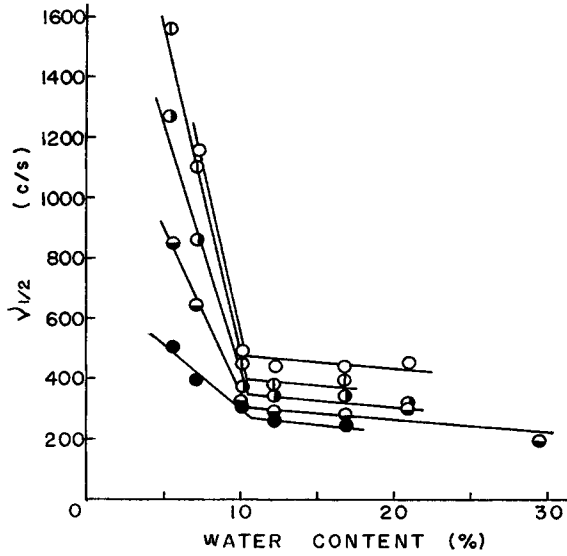


Fig. 3. Relationship between width at half-value and water content in cotton sample at various temperatures: (●) 40°C; (◐) 26°C; (○) 0°C; (○) -15°C; (○) -30°C.

samples, and differential energy of water binding in the low water content region is extremely sensitive to the measuring temperature.

It is apparent from Figures 1, 2, and 3 that the lower the measuring temperature, the more accurately the low water content region showing strong differential energy of water binding can be determined. Such relationships at 0°C are shown for unbeaten DP, cotton, and unbeaten SCP in Figure 4.

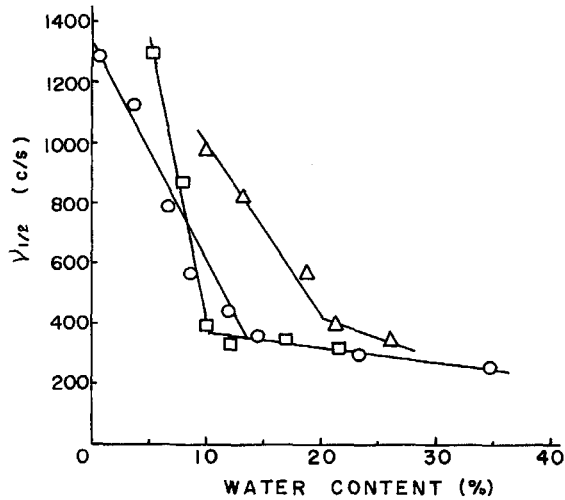


Fig. 4. Relationship between width at half-value and water content at 0°C: (O) unbeaten DP; (□) cotton; (Δ) unbeaten SCP.

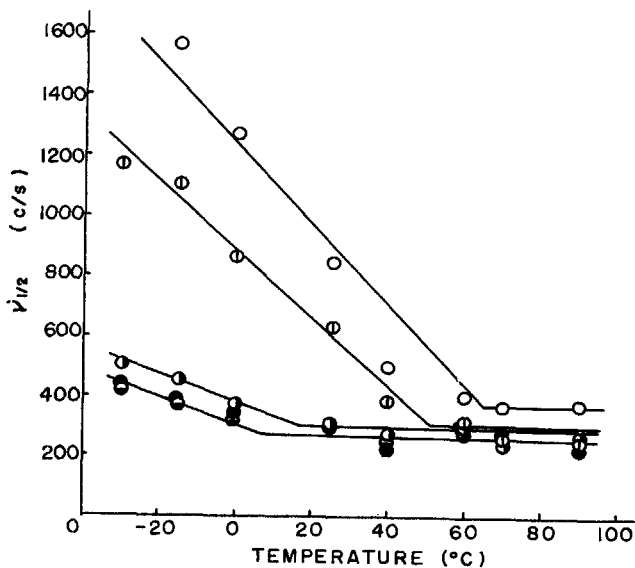


Fig. 5. Effect of sample temperature on width at half-value in cotton samples of various water contents: (O) 5.42%; (⊙) 7.42%; (●) 10.4%; (◐) 12.4%; (●) 16.9%.

The position of the inflection point and the slope of the straight line are characteristic of each sample, and the state of bound water determined in this manner seems to point out clearly the characteristics of the sample.

Changes of the width at half-value with temperature are shown for the cotton samples of varying water contents in Figure 5. Two temperature regions showing different states of water binding are distinctly observed for

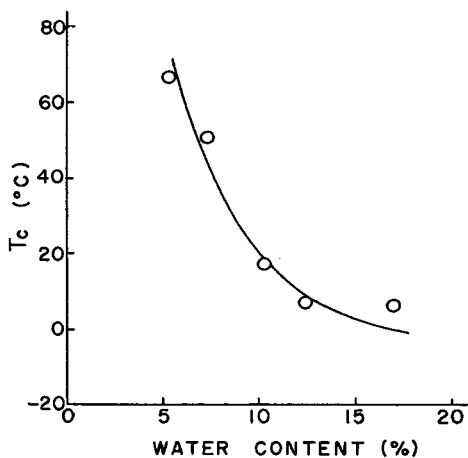


Fig. 6. Relationship between T_c and water content in cotton samples.

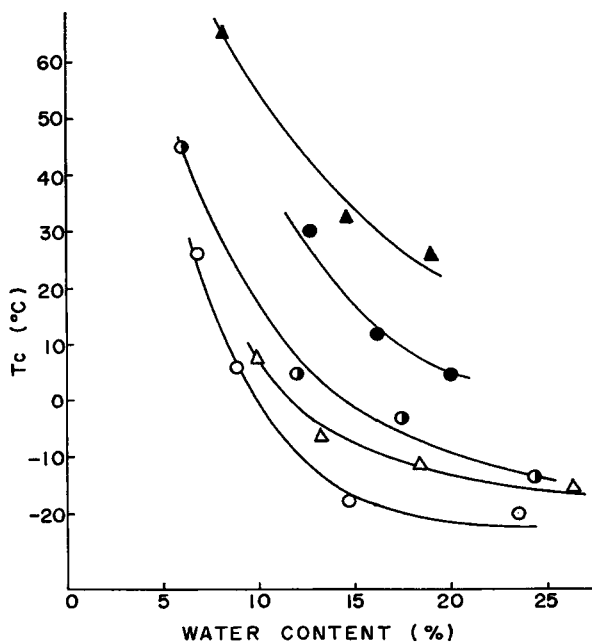


Fig. 7. Relationship between T_c and water content: (○) unbeaten DP; (●) beaten DP (44°SR); (●) beaten DP (64°SR); (Δ) unbeaten SCP; (▲) beaten SCP (80°SR).

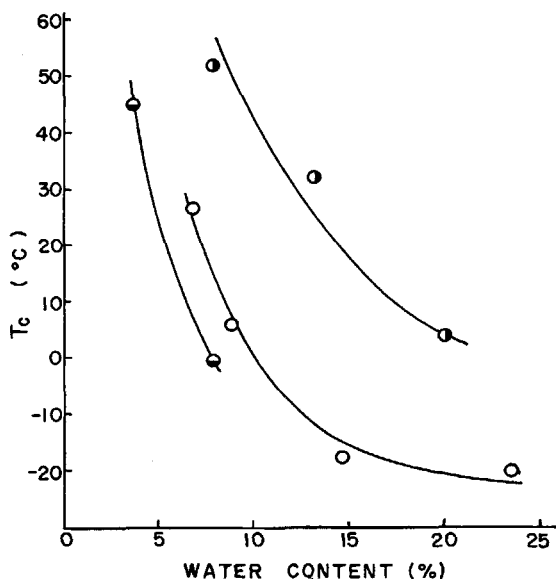


Fig. 8. Relationship between T_c and water content: (O) unbeaten DP; (●) DP swollen by sodium hydroxide; (⊙) DP hydrolyzed with hydrochloric acid.

each sample, and the temperature at the boundary is designated as T_c . Woodward et al.² studied broad-line NMR spectra of various polyamides containing D_2O as well as H_2O and reported on the presence of a certain temperature range for each sample where the line widths of the NMR spectra become narrower. The temperature T_c tends to move higher as the water content increases, and the relationship between T_c and the water content of the sample may be expressed as in Figure 6. That is, the lower the water content of a given region becomes, the greater the changes in T_c tend to become. In connection with such a relationship, it is known that the glass transition temperatures of cellulose,³ nylon 66,^{4,5} and the like are influenced markedly by small changes in water content, and the knowledge obtained in the present NMR spectroscopic study hints at the occurrence of a similar phenomenon. Furthermore, Hatakeyama and Kanetsuna⁶ determined the glass transition temperature of cellulose by means of differential scanning calorimetry and reported that the glass transition temperature of moist cellulose is considerably lower than that of air-dried sample.

The relationships between T_c and water content are shown for samples of DP and SCP in Figure 7. Each of the samples shows the same tendency as in the case of cotton, but the position of the curve in this figure varies greatly depending upon the sample; T_c of SCP is higher than that of DP when compared at the same water content, and T_c rises as the beating treatment progresses for the same pulp.

As already mentioned, T_c designates the boundary temperature at which water molecules become bound by cellulose in the cellulose sample of a given

water content. Below this temperature, the water molecules forcing their way into amorphous cellulose molecules destroy the cellulose-cellulose hydrogen bonds and form new water-cellulose hydrogen bonds. As a result, the water is in a state devoid of freedom of motion. Consequently, in NMR spectroscopy, the relaxation time of protons in such water becomes longer and the line width is larger compared with free water. Above T_c , on the other hand, the hydrogen bonds between cellulose and water in the system can be broken sufficiently by thermal motion, and the water in the system is expected to have a fairly large degree of freedom. Accordingly, the width at half-value of the NMR spectra in this case is very close to that of free water; moreover, the bonds between cellulose molecules in the amorphous portion are considered to be extremely weakened. From the above discussion, T_c is understood to represent the glass transition temperature itself of the cellulose-water system.

The foregoing relationships are tested in Figure 8 on samples which have been hydrolyzed with hydrochloric acid as well as treated with sodium hydroxide; T_c tends to rise slightly after sodium hydroxide treatment but falls after hydrolysis with hydrochloric acid. An increase in swelling of the former sample is regarded as the main cause of the rise of T_c , whereas a decrease in the amorphous portion of the latter sample seems to be mainly responsible for the fall of T_c .

A comparison of the above characteristics among various cellulose samples should be an interesting object of study.

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