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Studies of Water Adsorbed on Cellulosic Materials by a High Resolution NMR Spectrometer

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Synopsis

A study of water contained in cellulose samples, softwoods dissolving pulp (DP) and hardwoods semichemical pulp (SCP) by a high resolution NMR spectrometer indicated the presence of two regions, one where the width at half value decreased rapidly with increasing water content and the other where the width at half value decreased slowly. As a result of a treatment for increasing the hydrophilicity of cellulose fibers such as beating, swelling by sodium hydroxide, and hydrolysis with hydrochloric acid, the differential energy of water binding increased in the low water content region, whereas it either did not change or decreased in the high water content region in spite of an increase in the amount of water, which is subject to the influence of the cellulosic materials. A comparison of different cellulosic materials showed that the differential energy of water binding of SCP was larger than that of DP. Moreover, an investigation of the relationship between the width at half value and the temperature indicated that different temperature ranges exist regarding binding of water, and such ranges are affected greatly by the degree of beating and the water content of the sample.

INTRODUCTION

Water adsorbed on cellulose fibers is generally classified into bound water and free water. Although no clear definition is given to these terms nor standard methods of analysis are available at present, bound water is inseparably bound with cellulose molecules and appears to participate directly in the swelling of fibers. On the other hand, free water is present on the surface of fibers or in capillaries of the fiber structures and can be liberated substantially by the mechanical application such as centrifugal force.

The amount of bound water in cotton cellulose samples is generally in the order of 15%.[1] We earlier reported that the amount of water remaining after centrifugation of the water-soaked samples varied widely from 50 to 200% of the oven-dry samples depending upon the state of samples.[2] Such adsorption water has been analyzed by broad line NMR[3,4] or the width at half value of high resolution NMR absorption spectrum.[5] The object of our study was to examine by a high resolution NMR spectrometer how the state of bound water in the cellulose samples varies depending

upon the kind of cellulose or the treatment to which the cellulose samples are subjected.

EXPERIMENTAL

Commercial softwoods dissolving pulp (DP) and hardwoods semichemical pulp (SCP) were used as the cellulose samples, and they were beaten to varying degrees by a small laboratory beater, or treated with a 12% aqueous solution of sodium hydroxide at room temperature for 60 min followed by washing with distilled water, or hydrolyzed with 2 *N* hydrochloric acid at 100°C for 3 hr. The resultant moist samples were dehydrated to given water contents, each of the samples was packed closely in a sample tube, the high resolution NMR absorption spectrum was measured, and the dispersion of absorption was shown by the width at half value. A Japan Electron Optics Laboratory NMR spectrometer Model TNM-C-60HL with its accessories for varying temperature was used for measurements mostly under the following conditions, with variations in temperature as occasion demanded; resonance frequency, 60 Mc; sweep rate, 90 ppm/2.5 min; RF level, 40 db; sample temperature, 26°C (room temperature).

RESULTS AND DISCUSSION

Odajima,[5] previously observed that the greater the amount of water in mulberry paper, the larger was the decrease in the width at half value of the NMR absorption spectrum of water. We have also observed this tendency in the unbeaten DP samples; as the water content increased from 12.5 to 34.7 to 84.4%, the width at half value decreased from 414.1 to 244.2 to

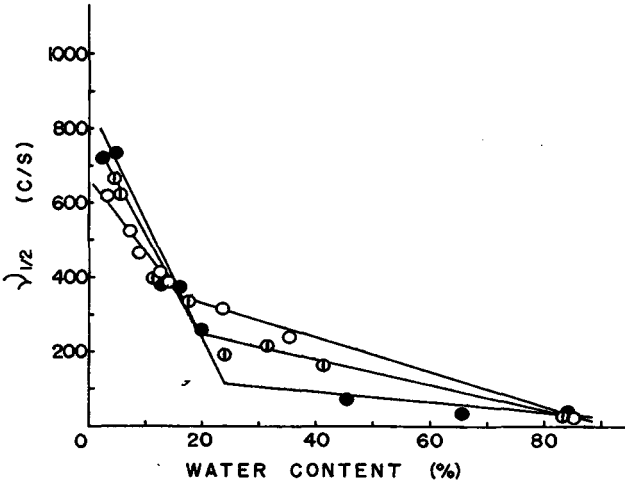

Fig. 1. Relationship between the width at half value and the water content in DP samples. (○), unbeaten pulp (13°SR); (◑), beaten pulp (44°SR); and (●), beaten pulp (64°SR). Sample temperature, 26°C.

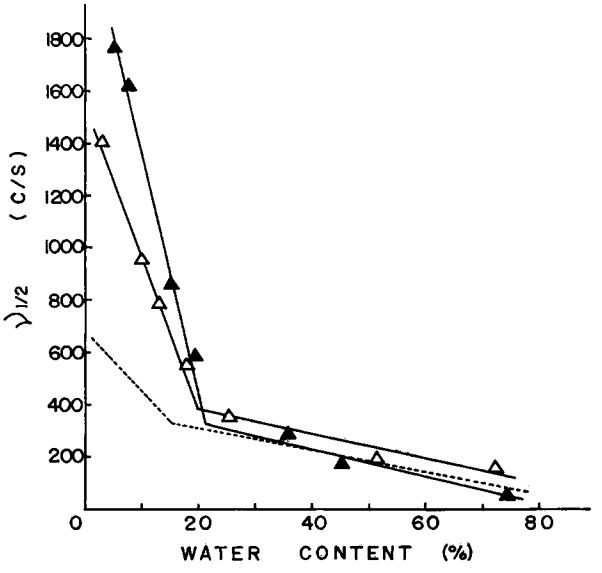

Fig. 2. Relationship between the width at half value and the water content in SCP samples. (△), unbeaten pulp (18°SR); (▲), beaten pulp (80°SR). A dotted line represents unbeaten DP sample. Sample temperature, 26°C.

19.2 c/s. The relationship between the width at half value and the water content in the beaten DP samples is shown in Figure 1. It is seen that this relationship can be divided into two straight lines of different slopes, one representing the section where the width at half value decreases rapidly as the water content increases, and the other section where the width at half value decreases slowly. When a comparison is made at the same water content, a larger width at half value of the absorption spectrum means a larger differential energy of binding between water and the cellulosic materials. In the low water content region below the point of inflection of the above-mentioned line, the width at half value showed a tendency to increase as the beating advanced; that is, the beating effects cleavage or division of cellulose fibers into fibrils mainly by a mechanical action and, as a result, the differential energy of binding between water and the cellulose fibers tends to increase.

In the high water content region above the point of inflection, however, the differential energy of binding between water and cellulose rather decreased as the degree of beating increased. Such a phenomenon is contrary to the view generally held that the beating increases the hydrophilicity of cellulose fibers and the differential energy of binding between water and cellulose. Our interpretation of this is as follows. The beating undoubtedly effects division of fibers into fibrils with the resultant increases in the surface area[6,7] and the hydrophilicity of the fibers. Consequently, a considerable increase in the amount of water which is in contact with the fibers is expected. However, the differential energy of water binding is

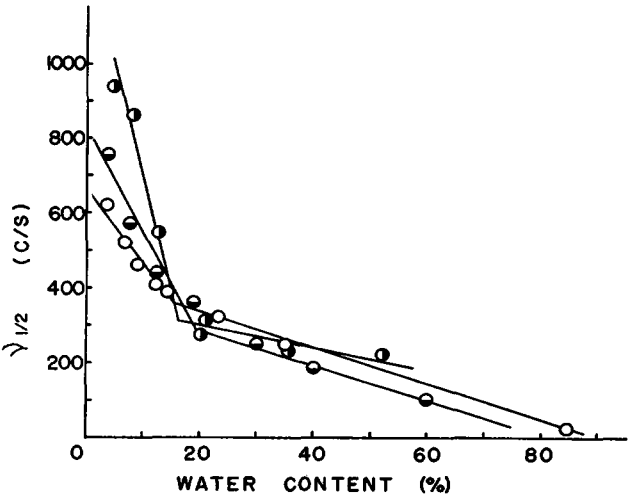

Fig. 3. Effect of the swelling by sodium hydroxide and the hydrolysis with hydrochloric acid on the width at half value. (○), unbeaten DP sample; (◑), DP swollen by sodium hydroxide; and (◒) DP hydrolyzed with hydrochloric acid. Sample temperature, 26°C.

not necessarily proportional to such quantities as above, and it may rather disappear when the amorphous region of fibers is destroyed and liberated properly by the beating. On the other hand, the differential energy of water binding was seen to increase rapidly when dehydration of the sample advanced beyond a certain point into the low water content region, and this is probably because a cohesive force working between cellulose molecules increases greatly and the differential energy of binding of water contained in them increases.

The same relationship as above is shown for SCP in Figure 2. The effect of the beating on the differential energy of water binding was essentially the same as for DP. A comparison of the different cellulose samples showed that SCP had in general a larger differential energy of binding toward water than DP.

The relationship between the width at half value and the water content are shown for the samples hydrolyzed with hydrochloric acid, as well as swollen by sodium hydroxide in Figure 3. As is evident from Figure 3, the treatment with sodium hydroxide notably increased the differential energy of water binding in the low water content region, but the state of bound water in the high water content region was substantially the same as that in unbeaten pulps. An increase in the differential energy of binding in the low water content region is considered to be due to enhanced swelling of the amorphous portion of the cellulose sample, by sodium hydroxide in the same manner as SCP shows a larger differential energy of water binding than DP because of larger swelling of SCP. The effect observed in the high water content region is probably explained by the observation re-

ported previously that, contrary to beating, swelling of the cellulose sample by sodium hydroxide does not virtually effect mechanical destruction of the fiber structures.[2] On the other hand, the differential energy of water binding of microcrystalline cellulose, which had been obtained in about 90% yield by hydrolysis in the presence of hydrochloric acid, became slightly

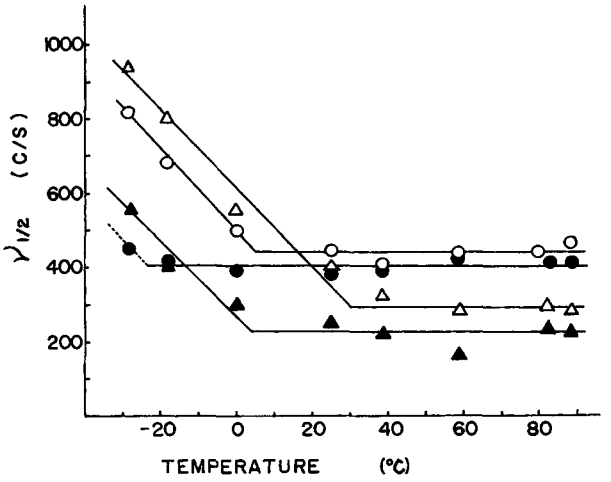

Fig. 4. Effect of the sample temperature on the width at half value. (○), DP (13°SR), water content, 8.90%; (●), DP (13°SR), water content, 14.6%; (△) DP (64°SR), water content, 12.7%; and (▲) DP (64°SR), water content, 20.0%.

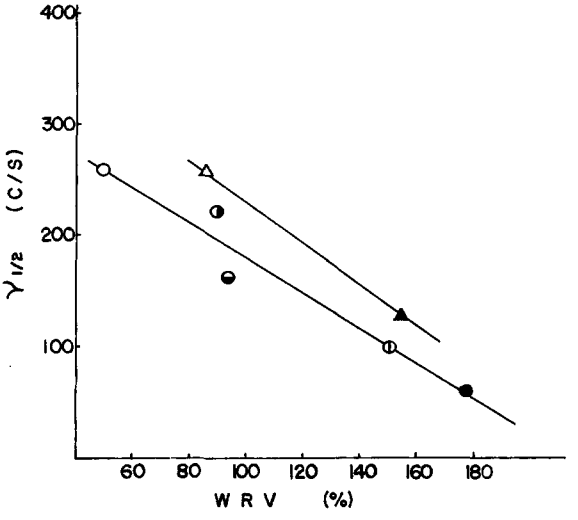

Fig. 5. Relationship between the width at half value and the water retention value. (○), DP (13°SR); (◑), DP (44°SR); (●), DP (64°SR); (◑), DP swollen by sodium hydroxide; (◒), DP hydrolyzed with hydrochloric acid; and (△) SCP (18°SR); (▲), SCP (80°SR). The water retention value expresses in percent against the oven dry sample.

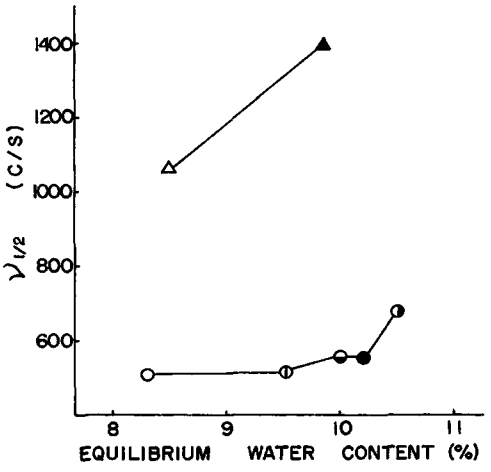

Fig. 6. Relationship between the width at half value and the equilibrium water content. (○), DP (13°SR); (◑), DP (44°SR); (●), DP (64°SR); (◑), DP swollen by sodium hydroxide; (◒), DP hydrolyzed with hydrochloric acid; (△), SCP (18°SR); and (▲), SCP (80°SR). The equilibrium water content obtained by placing a dry fiber in relative humidity of 65%.

larger than that of unbeaten pulps in the low water content region but smaller in the high water content region, and the results obtained were similar to those of beaten pulps as shown in Figures 1 and 2. The discussion given above on the beaten samples will also hold true of a phenomenon such as this.

Width at half value measured at various temperatures of the DP sample whose water content is near the point of inflection in the low water content region are shown in Figure 4. Plots of the width at half value of the beaten as well as unbeaten samples against temperature are distributed on two straight lines, and the width at half value rose rapidly when the temperature fell below a certain point, but did not change appreciably above this point. Thus, a study by NMR shows the existence of temperature ranges where the states of bound water differ, and such ranges are evidently affected by the degree of beating and the water content of the sample. As shown in Figure 4, the point of inflection of a sample moved toward a higher temperature as the beating advanced and the water content decreased. It is known that the glass transition temperature of a cellulosic material falls rapidly as the water content increases,[8] and the temperature corresponding to the point of inflection here seems to be closely related to the glass transition temperature of the cellulose–water system. The degree of beating of the sample is observed to affect greatly the temperature corresponding to this point of inflection, and such an observation is considered to be significant in studying the relationship between cellulose and water.

The water retention value serves as a kind of indicator of the hydrophilicity of cellulose samples. The relationship between the water reten-

tion value and the width at half value of the NMR spectrum of the cellulose sample at such water content is shown in Figure 5. The cellulose sample which had been soaked in distilled water for 24 hr was dehydrated by centrifugation at 6700 *g*, and the water content at this point, expressed in percent against the oven dry sample, was taken as the water retention value. For both DP and SCP samples, the width at half value showed a tendency to decrease as the water retention value increased. Therefore, although the water retention value is supposed to give a quantitative relationship between cellulosic materials and water, it is observed that the value contributes rather negatively to the differential energy of water binding.

The relationship between the equilibrium water content obtained by placing a dry fiber successively in atmosphere of relative humidity of 65% and the width at half value, corresponding to this water content is shown in Figure 6. The equilibrium water content of the cellulose sample increased somewhat after various treatments, and the width at half value corresponding to such water content increased and the differential energy of water binding tended to increase. However, the differential energy of water binding of DP and SCP differ greatly from each other, and that of SCP was markedly larger when compared at the same water content.

Both the water retention value and the equilibrium water content are in effect indicators of the hydrophilicity of cellulosic materials, and each is evidently related to binding of water. It was made clear in the samples with water contents in their measurable range that the differential energy of water binding is inversely proportional to the water retention value, but is directly proportional to the equilibrium water content.

References

1. E. Ott, H. M. Spurlin, and M. W. Grafflin, *Cellulose and Cellulose Derivatives*, Part I, Interscience, New York, 1954, p. 399.
2. Y. Ogiwara and K. Arai, *Textile Res. J.*, **38**, 885 (1968).
3. T. Swanson, E. O. Stejskal, and H. Tarkow, *Tappi*, **45**, 929 (1962).
4. R. E. Dehl, *J. Chem. Phys.*, **48**, 831 (1968).
5. A. Odajima, *J. Phys. Soc. Japan*, **14**, 308 (1959).
6. L. V. Forman, *Tappi*, **33**, 444 (1950).
7. W. L. Ingmanson and E. F. Thode, *Tappi*, **42**, 29, 74, 83 (1959).
8. K. Tsuge and Y. Wada, *J. Phys. Soc. Japan*, **17**, 156 (1962).

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