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The Determination of the Amount of Bound Water Within Cellulosic Gels by NMR Spectroscopy

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Synopsis

It has been shown that the NMR spectrum of moist cellulose is consistent with the idea that part of the water within the gel is destructured and bound to the accessible surfaces. A method for calculating the amount of bound water is presented, but because of experimental difficulties in obtaining an exact value for the spin-spin relaxation time of the protons in the bound water, only upper limits can at present be obtained for the amount of bound water. Accordingly, it is estimated that the amount of bound water does not exceed the following values: wood, 0.23 g/g; cotton, 0.15 g/g; two wood pulps, 0.30 and 0.33 g/g. The amount of bound water appears to approximate to a monomolecular layer upon all accessible surfaces, which suggests that the NMR technique might be used to determine the surface areas of the gels in the wet state.

INTRODUCTION

Considerable evidence has accumulated in the literature which indicates that part of the water within a moist cellulose gel exhibits properties which are markedly different from those of the rest of the water. In 1932, Filby and Maass[1] concluded from the high apparent density which could be calculated for cellulose when the volume was determined by the displacement of water that part of the water in the cellulose–water system had a higher density than that of free water. In the same year, Champetier[2] added cellulose to a solution of sodium thiosulfate and found that this resulted in a rise in concentration. He concluded that part of the water in a cellulose–water system was incapable of holding small ions in solution. In 1935, Stamm and Loughborough[3] calculated from calorimetric data that part of the water absorbed by cellulose was absorbed with the evolution of more heat than the remainder and surmised that this water was "bound" in some specific way to the cellulose surface. In later years, Magne and coworkers[4,5] found that a fraction of the water within moist cellulose was not frozen at temperatures well below the freezing point of water. Most of these investigations were carried out on cotton, and the experiments were repeated by many workers and yet there is a distinct lack of agreement upon the exact amount of bound water. One reason for this is that in each type of experiment, the result is dependent upon the conditions used. Thus,

in the "nonfreezing water" experiments, the results depend upon the temperature employed. In the "nonsolvent water" experiments using ionic solutes, the value varies with the concentration of the solute used. In a review of these and other methods, Boesen has suggested that 0.12 g bound water per g cellulose was the best average value for cotton.[6]

The advent of the idea that water should be regarded as an equilibrium mixture of strongly hydrogen-bonded clusters and monomeric molecules[7] shed new light on the nature of bound water. Ramiah and Goring[8] pointed out that a cellulose surface was a structure breaker for water and as such would be covered with a layer of monomeric water. Since the monomeric water is believed to have a higher density than the clustered water molecules, new credence was given to the earlier observations of Filby and Maass[1] whose evidence had, in the intervening years, been explained away on other grounds.[9] More recently, the presence of water of high density has been reported near the surfaces of nylon, dacron, and glass fibers.[10]

Ramiah and Goring[8] also found that the thermal expansion of pellets of cellulose immersed in water was apparently greater than that of the dry solid. This too they attributed to a change in the cluster–monomer equilibrium of the water brought about by the presence of the cellulose. Nemethy and Scheraga[11] had concluded earlier that monomeric water had a greater thermal expansion coefficient than that of clustered water. From measurements of thermal expansivity, Neal and Goring[12] estimated the amount of destructured water in various forms of cellulose. Among their values were 0.04 g/g for cotton linters, 0.06 g/g for wood pulp, and 0.10 g/g for cellophane.

The application of nuclear magnetic resonance (NMR) spectroscopy has also furthered the concept of bound water. The NMR spectrum of moist cellulose exhibits a peak due to the protons in water superimposed upon a very much wider peak due to the protons in cellulose.[13–18] The water peak is broader than that shown by free water, a fact which has been interpreted in terms of some of the water molecules being restricted in mobility owing to their proximity to the surface of the solid material. The amount of broadening (line width) has been plotted as a function of moisture content and a point of inflection observed in the curve.[18] The moisture content at this point has been taken to be the quantity of less mobile water and has been found by Ogiwara to be about 0.2 g/g of cellulose for two different wood pulps. In addition to cellulose, line broadening of the NMR spectrum of water protons is brought about by muscle tissue,[19] various other biological materials,[20] and hydrated silica gel.[21]

Examining the NMR spectrum of moist cellulose ourselves, we have observed that not only is the peak of water broadened by the presence of cellulose, but that it has moved to higher magnetic fields (Fig. 1). This "shift" appears not to have been observed by previous workers on cellulose although it has been reported for the water–keratin system.[22] It has long been recognized in NMR spectroscopy that a shift of a proton to higher fields can be due to the breaking of hydrogen bonds. In the case of pure

water, there is a shift toward higher fields when the temperature is raised.[23] In terms of the flickering cluster theory of water,[7] this shift is believed due to the displacement of the equilibrium between the strongly hydrogen-bonded clusters and the monomeric molecules, in favor of a higher concentration of monomeric molecules of water.[24] Coupling this interpretation of the shift to the previous one for the broadening of the peak, the NMR spectrum is quite consistent with the idea that not only is part of the water in moist cellulose bound to the surface, as concluded by workers with other techniques, but, in agreement with Ramiah and Goring, this water is destructured. The destructured water is presumably bound to the cellulose by hydrogen bonds; however, the direction of the shift indicates that these are weaker than the hydrogen bonding system in the clusters. It is of interest that the differential heat of wetting of cellulose at zero moisture con-

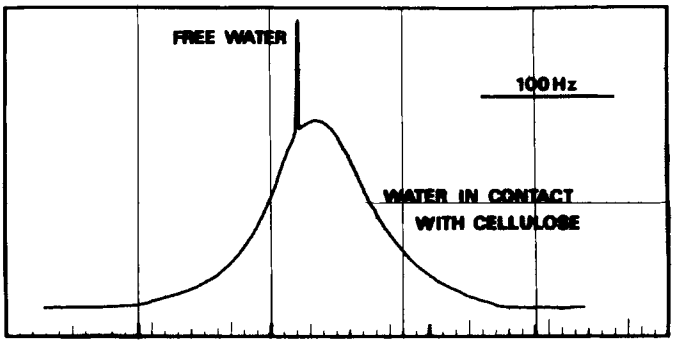

Fig. 1. High-resolution NMR spectra of moist cellulose and free water (reference distilled water). The compound spectrum was obtained by inserting a fine glass capillary tube filled with water into the NMR tube containing the moist cellulose. This technique permits easy observation of the chemical shift.

tent is about 5.0 kilocalories per mole of water,[3] which is of the right order for the breakage of, on the average, one hydrogen bond per molecule of water added. However, it is to be noted that this is the net energy resulting from not only the breakage of hydrogen-bonded clusters of water and the formation of water–cellulose hydrogen bonds, but also the breakage by wetting of cellulose–cellulose hydrogen bonds in the dry cellulose.

Thus, the NMR spectrum of moist cellulose is in accord with current ideas on the existence and nature of bound water. Until now, only Ogiwara has attempted to deduce the amount of bound water by this technique. In the present communication, we describe how the amount of water bound by cellulose may be calculated from the high-resolution NMR spectrum. The method is based on that used by Bermudez for hydrated silica gel.[21] It does not depend upon the detection of a slight inflection in a curve as does the work of Ogiwara[18] and Odajima.[13]

THEORY

The "mobility" of a proton in NMR spectroscopy is correlated to its transverse relaxation time (T_2) which can be calculated from the line width at half-height ($\nu_{1/2}$) according to the equation

$$T_2 = \frac{1}{\pi \nu_{1/2}}. \tag{1}$$

Let us now evoke a two-state theory for the water molecules in the cellulose–water system and let T_{21} and T_{22} be the relaxation times of the protons in the bound water molecules and the normal equilibrium mixture of structured and unstructured water, respectively. Fedotov[25] has shown that there is a rapid exchange between the bound molecules and those away from the surface, but only a slow exchange of the protons of water with the protons of the hydroxyl groups of plant cell walls. Therefore, the NMR absorption line arises from only the water protons, and the average relaxation time experimentally observed in the cellulose–water system (T_2) is given by[26]

$$\frac{1}{T_2} = P_1 \frac{1}{T_{21}} + P_2 \frac{1}{T_{22}} \tag{2}$$

where P_1 and P_2 are the probabilities that at a given moment a proton is at or away from the surface.

Now the value of T_{22} (relaxation time of bulk water) is of the order of 3.0 sec, while from the experimentally observed broadening of the line of water in the presence of cellulose, T_2 is of the order 10^{-3} sec; and we may assume that the relaxation time of bound water is even less than this. Bermudez used a value of $T_{21} = 2 \times 10^{-4}$ sec for the water bound to silica gel.[21] Therefore, $1/T_{22}$ is negligible compared with either $1/T_2$ and $1/T_{21}$, and hence the second term on the right-hand side of eq. (2) may be neglected. Introducing $P_1 = [H_2O]_1/[H_2O]_T$, where $[H_2O]_1$ is the concentration of bound water in the sample at a total moisture-content of $[H_2O]_T$, eq. (2) becomes

$$T_2 = \frac{T_{21}}{[H_2O]_1} \times [H_2O]_T. \tag{3}$$

According to this equation, as long as $[H_2O]_1$ remains constant, we should expect a linear relationship between the observed relaxation time T_2 and the moisture content. Furthermore, the linear plot should pass through the origin. However, if a plot of T_2 versus $[H_2O]_T$ is made starting at high moisture contents, we should expect the linear relationship to hold with reducing moisture content only as long as the cellulose–water system is above the fiber saturation point, that is, while the water which is being removed is from the spaces exterior to the cell walls. In drying wet cellulose fibers, the water exterior to the cell walls is usually removed first because of the larger diameter of the capillary spaces that contain it compared to cell wall pores.[27] Once the moisture content is reduced below the fiber

saturation point, it has been shown that the cell walls progressively collapse and the interior surface area exposed to water becomes correspondingly reduced.[28] We would therefore expect, with a reduction of the moisture content below the fiber saturation point, a reduction in $[H_2O]_1$ and a departure of the curve of T_2 versus $[H_2O]_T$ from linearity. Exactly how the plot of T_2 versus $[H_2O]_T$ should vary at moisture contents below the fiber saturation point is uncertain since the variation of the amount of exposed surface at these moisture contents is by no means well established. However, as very low moisture contents are attained, it might be assumed that all the remaining water is bound water, in which case eq. (3) reduces to

$$T_2 = T_{21} \text{ when } [H_2O]_T \rightarrow [H_2O]_1 \rightarrow 0. \quad (4)$$

That is, a plot of T_2 versus $[H_2O]_T$ might be expected to intercept the T_2 axis at $T_2 = T_{21}$.

Our experimental program to obtain the amount of bound water was therefore to plot T_2 as determined from the experimentally observed line broadening, as a function of moisture content for several fibrous cellulose–water systems. From the linear section of the curve, we obtained the quantity $T_{21}/[H_2O]_1$; and by substitution of T_{21} from the intercept, we obtained a value of the amount of bound water in the saturated fibers.

EXPERIMENTAL

Samples

Experiments were carried out on four samples of cellulosic material: finely ground sprucewood, two "never dried" pulps of the same wood, and cotton linters. The two pulps were a sulfite pulp of 76.5% yield and a kraft pulp of 63.8% yield.

All samples were soaked in distilled water for two days and then thoroughly washed in additional distilled water in order to remove soluble material, particularly paramagnetic impurities. In one case, a sample was given a further treatment with ethylenediamine tetraacetate solution to complex possible remaining paramagnetic ions and was rewashed; however, the spectrum then observed was identical to that observed before this additional treatment.

Spectroscopy

The samples were brought from a very wet state to the required moisture content either by centrifugation or, for the attainment of a very low moisture content, by conditioning in an atmosphere of given humidity. Once conditioned, each of the samples was packed as tightly as possible in the NMR tube. Variations in packing proved not to alter the spin-spin relaxation time; but the better the packing, the greater the intensity of the signal and therefore the higher the precision of the measurements. The tubes (4.3 mm internal diameter) were kept stoppered until after the NMR

analysis when an exact moisture content was determined by weighting the contents of the tubes before and after oven drying at 105°C.

The instrument used was a Varian T60 NMR spectrometer and the conditions employed were a resonance frequency of 60 Mc/sec, a radio frequency power level of 0.05 dB, a sweep rate of 1 Hz/sec, and a spinning rate of 30 rps. Because the peak width at low moisture contents was several times the normal scanning range (500 Hz), the spectrum at low moisture contents was recorded by four successively offset scans to make an effective range of 2000 Hz. All experiments were carried out at room temperature.

Fiber Saturation Points

The fiber saturation points of the pulps were determined by the solute exclusion technique using a previously established procedure.[27] Pharmacia's dextran fraction Dextran 2000 was used as the totally excluded molecular probe.

RESULTS AND DISCUSSION

Figure 2 shows the experimentally determined line width $\nu_{1/2}$ for the various samples as a function of moisture content. Owing to the scatter of the points, it is impossible to detect the slight inflections in these curves as reported by Ogiwara et al.[18] However, if, using the same data, the

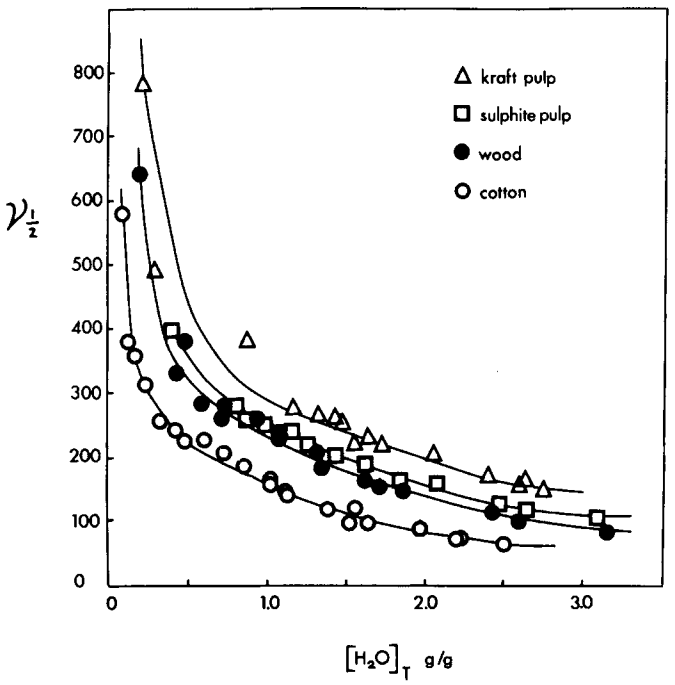

Fig. 2. Plots of line broadening ($\nu_{1/2}$) as a function of total moisture content ($[H_2O]_T$) for the four samples examined.

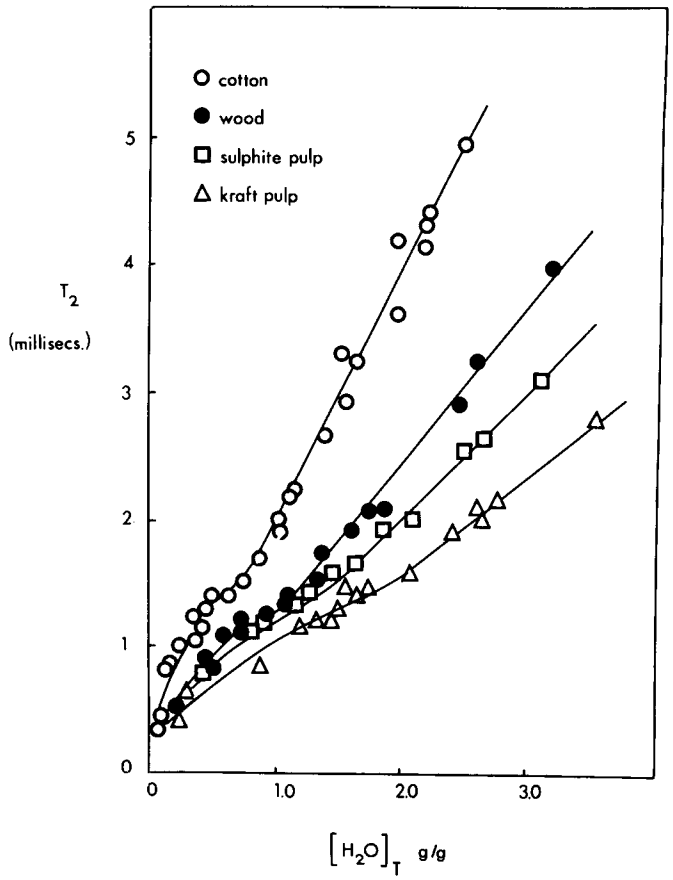

Fig. 3. Plots of the observed spin-spin relaxation time (T_2) as a function of total moisture contents for the four samples examined.

relaxation time T_2 is calculated, by using eq. (1), and this quantity rather than $\nu_{1/2}$ is plotted against moisture content, close to linear plots are obtained above the fiber saturation point (Fig. 3). Below the fiber saturation points, for reasons surmised in the previous section, the plots deviate from linearity and appear to converge at a common intercept on the T_2 axis.

The slopes of the plots in Figure 3 at moisture contents above the fiber saturation point are well defined, and it is readily possible to calculate the ratio $T_{21}/[H_2O]_1$ for each of the substances examined. However, in order to calculate the amount of bound water from these ratios, it is necessary to have a value of T_{21}. We have postulated that the intercept of the plots in Figure 3 should give this quantity, but it is seen that this cannot be obtained with any great precision. The curves appear to approach the y-axis rather steeply, and due to the difficulties in both obtaining uniform low moisture contents and in measuring the broadening at these moisture contents, there is scatter in the data. Accordingly, we have taken the

TABLE I
Experimental Results on Gels Examined

Substance	Slope of Fig. 3 $T_{21}/[H_2O]_1$	Maximum value of bound water, g/g[a]	Fiber saturation point, g/g
Cotton	1.98×10^{-3}	0.15	0.50
Wood	1.28×10^{-3}	0.23	0.45
Sulfite pulp	1.00×10^{-3}	0.30	1.34
Kraft pulp	0.95×10^{-3}	0.33	1.66

[a] Calculated from slope of Fig. 3 using $T_{21} = 0.3 \times 10^{-3}$ sec.

lowest experimental measurement of T_2 as the maximum possible value of T_{21} (0.3×10^{-3} sec) and substituted this into the values for the slopes at high moisture content to give us maximum estimates for the bound water. The value of 0.3×10^{-3} sec is of the same order as the 0.2×10^{-3} used by Bermudez for the relaxation time of water bound to silica gel.[21]

The results are given in Table I where it is seen that the amount of bound water varies from sample to sample and is only a fraction of that within the fiber walls (the fiber saturation point). As maximum amounts of bound water, the results satisfactorily encompass those reported by others where a comparison can be made. When the variability of wood pulp samples is taken into account, our finding of 0.3 g/g for wood pulp can be considered reasonably close to that (0.2 g/g) reported by Ogiwara. But our value is much higher than the 0.06 g/g reported by Neal and Goring.[12] By a similar factor our result for cotton linters (0.15 g/g) is higher than that of Neal and Goring for the same material (0.04 g/g). However, as pointed out by these workers,[12] their absolute values for destructured water are very dependent upon which values they take from the literature for certain constants—particularly that of the specific volume of destructured water (v_u). Similarly, our values are very much dependent upon the magnitude of the relaxation time of bound water (T_{21}). Nevertheless, our result is closer to the average for cotton (0.12 g/g) as obtained by other methods which do not involve NMR spectroscopy or the structure of water.

Several authors have correlated the amount of bound water to the number of accessible hydroxyl groups in cellulose, feeling that perhaps these groups hold the water by hydrogen bonding. The fraction of hydroxyl groups which is accessible to water is readily found from the number which can be exchanged in reaction with deutrium oxide. For cotton the fraction of the hydroxyl groups which are accessible is well established at 0.40. Since there are three hydroxyl groups per anhydroglucose unit in cellulose, the addition of one water molecule per hydroxyl group can be calculated to result in $0.40 \times 3 \times 18/162 = 0.14$ g/g of bound water in cotton (18 and 162 are the molecular weights of water and anhydroglucose, respectively). This theoretical value is close to our maximum value for cotton and the average value reported by Boesen.[6]

It may also be shown that the amount of bound water calculated by the NMR technique corresponds approximately to this water existing as a monomolecular layer upon all accessible surface area. The area covered by a single water molecule may be taken as $(18\ v_u/N)^{2/3}$, where 18 is the molecular weight of water, v_u is the specific volume of the water, and N is Avogadro's number. Taking 0.90 cc/g for the specific volume of the water[11] (assuming it to be destructured), we have 9.0 Å^2 for the area covered by a single adsorbed molecule, or 3000 m^2 for the area of a gram of water spread out as a monomolecular layer. Multiplying the amounts of bound water by the factor 3000, we obtain values for the surface area of our samples which correlate well with the surface areas which can be calculated

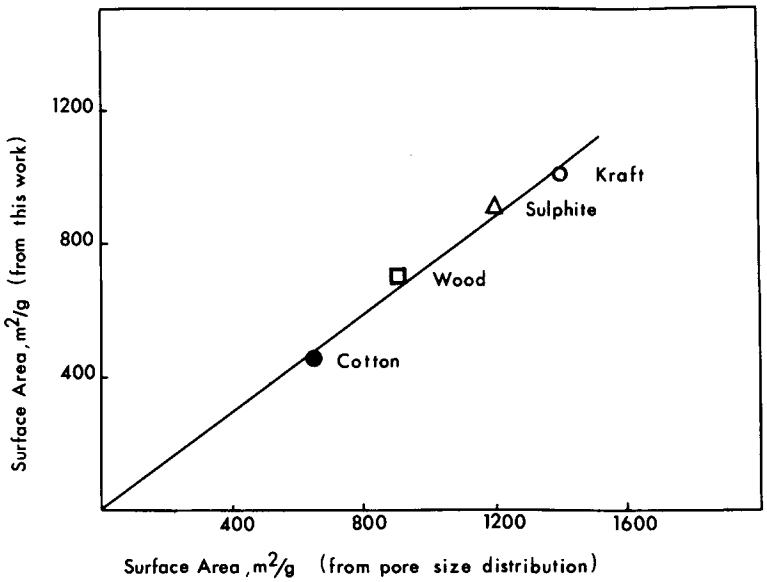

Fig. 4. Surface areas as calculated from amount of bound water correlate linearly with those calculated from pore size distribution.

from the pore distributions of the samples[29,31] by using a previously published method of calculation.[30] The correlation is shown in Figure 4. Although the absolute values of surface area obtained by the two methods differ, the agreement is surprisingly close considering the wide difference in approach of the two methods in this relatively unexplored field of surface area determination in the wet state.

The importance of surface area is well illustrated in the comparison of our results on cotton and wood. Despite the fact that because of its different composition wood has fewer hydroxyl groups per unit weight, it possesses more bound water than cotton. The two materials have approximately the same pore volume (fiber saturation point); however, it has been shown that the pores in wood[29] are smaller in size than those in cotton.[31] By

virtue of this fact, wood has a greater surface area per unit weight than cotton. Ahlgren and Goring[32] have also demonstrated that a linear relationship exists between the amount of bound water and the surface area of various cellulosic samples.

Whether the hydroxyl groups cause the adsorption of water or whether the adsorption is due simply to the presence of surface is a cause for speculation and further work.

CONCLUSIONS

We contend that the NMR spectrum of moist cellulose is consistent with current ideas on the nature and amount of bound water. The amount of bound water appears to correspond to a monomolecular layer upon all accessible surface area—a fact which suggests that NMR might be used as a method for determining surface area in the wet state.

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