N.m.r. study of cellulose–water systems: Water proton spin–lattice relaxation in the rotating reference frame*

H. Peemoeller and A. R. Sharp
Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3
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A pulsed n.m.r. study of relaxation in the rotating reference frame was performed on cellulose samples with moisture contents (MC) ranging from 20.5% to 218%. The dependence of the spin–lattice relaxation time ($T_{1\rho}$) in the rotating frame on temperature in a sample hydrated to approximately the fibre saturation point (FSP) indicates that in this case water exists in two different environments or phases. The first phase consists of a small number of water molecules (< 1% of adsorbed water molecules in sample) tightly bonded to cellulose whereas the second phase consists of the remaining adsorbed water molecules which are more loosely attached. At room temperature exchange occurs between these phases at an intermediate exchange rate. For samples with $MC > FSP$ a third water phase was identified. From the dependence of $T_{1\rho}$ on the rotating field strength information about water molecule dynamics was deduced.

(Keywords: cellulose; nuclear magnetic resonance; relaxation; water dynamics)

INTRODUCTION

It is now generally agreed that water in contact with macromolecules has very different properties from those normally found in bulk water. Water affected in this way by macromolecules has gained the unfortunate name 'bound water' despite the fact that it can be highly mobile. In addition, many different definitions of this term have been used. Some of these definitions are given[1] by Berendsen in his review, each one being an operational definition valid for a particular experimental situation. Some experimenters define 'bound water' in terms of thermodynamic properties, others in terms of molecular dynamics and still others in terms of structural properties. Because there are no clear cut relationships between these different aspects of the properties of water, a wide variety of results have appeared for the amount of 'bound water' in some systems, giving rise to considerable confusion. For example, the amount of 'bound water' in water–cellulose systems has been reported[2,3] to range from 0.04 g water per g of cellulose to 0.33 g/g depending on the system studied and the technique used. In an attempt to resolve this discrepancy and elucidate the dynamics of water adsorbed on cellulose a detailed nuclear magnetic resonance (n.m.r.) study of several water–cellulose systems has been undertaken.

Several n.m.r. studies of spin–spin relaxation times (T_2) and spin–lattice relaxation times in the laboratory reference frame (T_1) of cellulose–water systems having various moisture contents (MC=(g of H_2O/g of cellulose) × 100) have been reported in the literature[3–7]. In this paper, measurements of spin–lattice relaxation times in the rotating reference frame ($T_{1\rho}$) are reported for several cellulose–water samples having $MC > 20\%$.

EXPERIMENTAL METHODS

Microcrystalline cellulose with average particle sizes of 20 microns was obtained from Sigma Chemical Company. The cellulose was used without further treatment.

Approximately 100 mg of the cellulose was added to a 6 mm o.d. n.m.r. sample tube of known weight. The dry weight of the cellulose was determined by taking the difference between the sample weight after it had been under a vacuum of $< 10^{-3}$ Torr for 12 h and the weight of the sample tube. The desired MC was obtained by adding the appropriate amount of water to the sample. The sample tube was then sealed. N.m.r. measurements were performed after the cellulose and water had been allowed to equilibrate for one week. In this manner samples were prepared with moisture contents of 20.5%, 39%, 49.9%, 200% and 218%.

Proton relaxation measurements were made at 17.1 MHz using a Spin–Lock Electronics Model CPS-2 pulsed NMR spectrometer. $T_{1\rho}$ was measured using the spin–locking pulse sequence[8]. N.m.r. signals were observed with a Tektronix model 475 oscilloscope and relaxation time measurements were made at $t = 100$ μs on the free induction decay (FID) using a narrow window (denoted as a '100 μs window'). All magnetization decay curves were exponential.

RESULTS AND DISCUSSIONS

In general, the association of water with cellulose may be discussed in terms of two hydration regimes. In the first

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regime all water molecules, on average, are hydrogen bonded to hydroxyl groups of the cellulose molecule. Assuming that one H_2O molecule is hydrogen bonded to each OH group means that each cellobiose unit has six H_2O molecules attached to it; this gives $MC = 36\%$. This value is similar to the fibre saturation point (*FSP*) (25% to 35% moisture content) found for wood cell walls, suggesting that the assumption of one H_2O molecule/cellulosic OH group is reasonable. In a cellulose powder, hydrogen bonding also occurs between molecular chains so that not all cellulosic OH groups are accessible to water. As a consequence the saturation of the cellulosic OH groups is expected to occur for $MC < 36\%$. The exact value depends on the molecular chain length and sample history.

The second hydration regime has $MC > FSP$. The additional water (above fibre saturation) is more loosely attached to the cellulose, likely through other water molecules directly attached to cellulosic OH groups.

Experiments were performed in each hydration regime and are discussed below.

Wet cellulose sample with MC = *20.5%*

Values of $T_{1\rho}$ at a rotating field strength $H_1 = 6.7$ G for the cellulose sample with $MC = 20.5\%$ are shown as a function of temperature in *Figure 1*. $T_{1\rho}$ appears to have a minimum at ~210 K and then increases with increasing temperature up to about 260 K according to an Arrhenius activation law with an apparent activation energy $E_a = (7.4 \pm 0.3)$ kcal mol^{-1}. As the temperature is increased further $T_{1\rho}$ reaches a maximum at ~300 K and then decreases with increasing temperature. This latter behaviour can be attributed to either (a) the existence of a second $T_{1\rho}$ minimum at a temperature greater than those

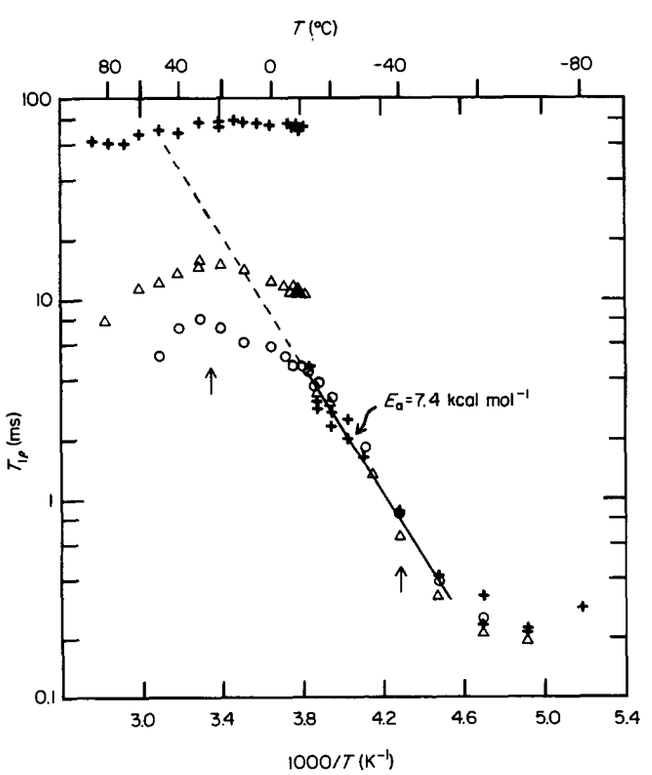

Figure 1 Temperature dependence of proton $T_{1\rho}$. The Larmor frequency is 17.1 MHz. $H_1 = 6.7$ G. The arrows indicate the temperatures at which $T_{1\rho}$ dispersion measurements were carried out. The solid and broken lines are discussed in the text: (○) $MC = 20.5\%$; (△) $MC = 39\%$; (+) $MC = 200\%$

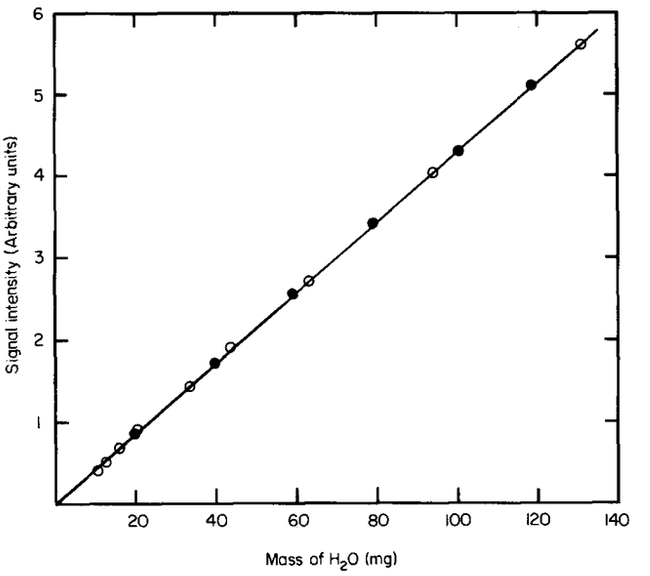

Figure 2 Signal intensity vs. mass of water in cellulose samples (○) and in bulk water samples (●). The solid line represents a linear least-squares fit to the bulk water data

studied here or (b) the existence of nuclear transfers between at least two phases[9,10] where the rate of such transfers increases with increasing temperature. Analogous behaviour with temperature was observed[11] for T_2 in a similar sample. This strongly suggests that case (b) is applicable here (see refs. 9 and 10 for details about T_2 temperature dependence in a system in which exchange predominates).

We attribute the above transfer effects to exchange of water molecules (protons) between a phase 'a' with intrinsic $T_{1\rho a}$ and a phase 'b' with intrinsic $T_{1\rho b}$. The rate for a molecule to leave phase a or b may be expressed in terms of the respective inverse lifetimes $1/\tau_a$ or $1/\tau_b$. The fractional sizes of the respective proton populations are P_a and P_b. In our experiments, at any particular temperature, only a single $T_{1\rho}$ value was observed which we associate with the a phase. The phase b protons were not directly observed because either (1) the size of phase b is too small or (2) $T_{2b} \ll 100\,\mu$s so that the phase b spins have dephased and are not observable at a 100 μs time window or (3) a combination of (1) and (2). *Figure 2* shows a plot of signal intensity *versus* mass of water in several cellulose samples and in several samples of bulk water. The solid line represents a linear least squares fit to the bulk water data. For a particular mass of water the signal intensity from water in cellulose is essentially the same as that from bulk water (*Figure 2*). Therefore, within the accuracy of the experiment, estimated at about 1% (*Figure 2*), all of the water in cellulose is observed. This means that $P_b \lesssim 0.01$ and $P_b \ll P_a$. In other words case (1) applies to these samples. It may be noted that from detailed balance ($P_a/\tau_a = P_b/\tau_b$) it is seen that the above also implies $\tau_b \ll \tau_a$. In addition it is evident from *Figure 1* that in the temperature range (above ~260 K), where exchange between phases comes into play, the small b phase has a considerable effect on the observed relaxation of the much larger a phase. This must mean that $T_{1\rho b} \ll T_{1\rho a}$. Then, the observed rotating frame spin–lattice relaxation rate for phase a ($1/T'_{1\rho a}$) is given[9] by

$$\frac{1}{T'_{1\rho a}} = \frac{1}{T_{1\rho a}} + \frac{P_b}{T_{1\rho b} + \tau_b} \qquad (1)$$

At temperatures below ~0°C it is expected that $T'_{1\rho a}$ values are not affected appreciably by nuclear transfer effects (*Figure 1*). This temperature region is denoted the 'slow exchange regime' in which the first term of equation (1) dominates so that $T'_{1\rho a} = T_{1\rho a}$. This, taken together with the fact that phase b protons were not observable, means that information about molecular dynamics in phase b in the slow exchange regime is not directly accessible in this study.

In the slow exchange regime the process which changes the water proton–water proton vector in phase a has $E_a = 7.4$ kcal mol^{-1} (*Figure 1*). This suggests that it requires two hydrogen bonds to be broken for a water molecule to assume a new position. Further details about the water molecule dynamics in this temperature range may be deduced from the dependence of $T_{1\rho a}$ on $\omega_1 = \gamma H_1$ where γ is the gyromagnetic ratio. *Figure 3* shows a plot of $1/T_{1\rho a}$ vs. $\omega_1^{1/2}$ at −40°C (also see *Figure 1*). The solid line represents a linear least squares fit of the data. The fact that $1/T_{1\rho a}$ is linear in $\omega_1^{1/2}$ indicates that the rotating frame spin–lattice relaxation at −40°C is dominated by intermolecular interactions[12]. In this case the straight line plot of $1/T_{1\rho a}$ vs. $\omega_1^{1/2}$ is given[12] by

$$\frac{1}{T_{1\rho a}} = -\frac{2\gamma^4 h^2 N}{80\pi D^{2/3}}\omega_1^{1/2} + \frac{1}{T_{2a}} \qquad (2)$$

where D is the translational diffusion constant, h is Planck's constant and N is the number density of protons. Using the bulk water proton density $N = 6.75 \times 10^{22}$ spins cm^{-3} and the slope of the solid line (*Figure 3*) in equation (2) we obtain $D = (2.0 \pm 0.2) \times 10^{-10}$ cm^2 s^{-1}. This value is about five orders of magnitude smaller than D of bulk water at room temperature suggesting that translational mobility of water molecules in phase a at −40°C is very limited.

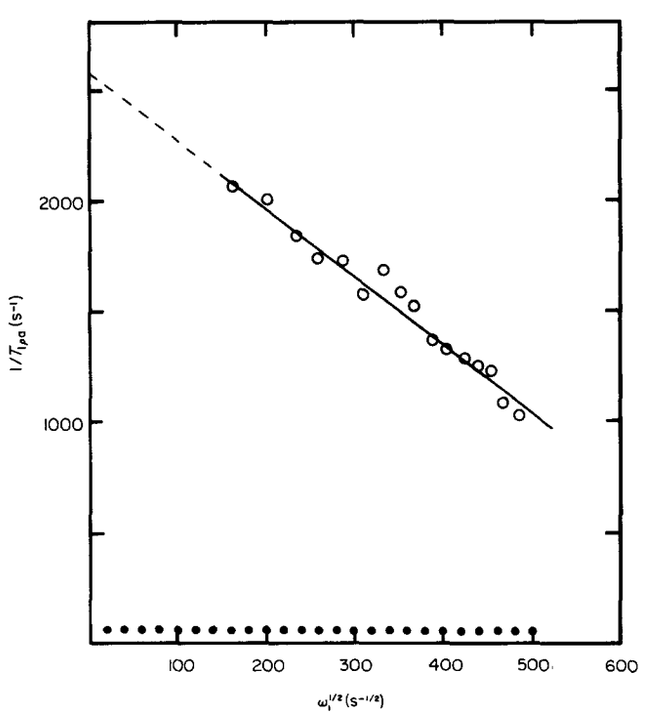

Figure 3 $1/T_{1\rho a}$ vs. $\omega_1^{1/2}$ in hydrated cellulose with $MC = 20.5\%$ at −40°C. The solid/broken line represents a linear least-squares fit to the data. The dotted line represents the estimated behaviour of $1/T_{1\rho a}$ at 25°C

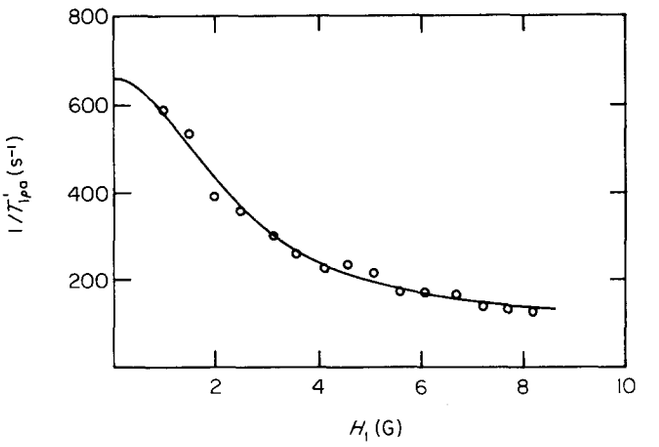

Figure 4 $1/T'_{1\rho a}$ dispersion plot in hydrated cellulose with $MC = 20.5\%$ at 25°C. The solid line was calculated using equation (4) with the parameters given in *Table 1*

It is interesting to compare the value of D for water found here to that of bound water in erythrocytes. In frozen packed erythrocytes at −55°C it was found[13] that for water $D = 0.85 \times 10^{-10}$ cm^2 s^{-1}. This is only about $2\frac{1}{2}$ times smaller than the value at −40°C for water bound to cellulose. Assuming that D of water bound to cellulose follows Arrhenius behaviour with $E_a = 7.4$ kcal mol^{-1} (*Figure 1*) we find that at 30°C the diffusion constant in the wet cellulose sample with $MC = 20.5\%$ has a value of 8×10^{-9} cm^2 s^{-1}. For bound water in erythrocyte membranes at 30°C it has been reported[14] that $D \sim 2 \times 10^{-9}$ cm^2 s^{-1} which is only four times smaller than the corresponding value in cellulose. The fact that the diffusion constants of bound water, at a particular temperature, in such different systems are of the same order of magnitude suggests that on a molecular level the water molecule does not 'see' these macromolecular surfaces as being very different.

In writing equation (2) it has been assumed that the only frequency dependent contribution to $1/T_{1\rho a}$ arises from intermolecular processes. The validity of this assumption can be checked by comparing the value of $T_2 = (390 \pm 10)$ μs, obtained from the intercept of the plot in *Figure 3* (also see equation (2)), to that found experimentally. At −40°C the measured $T_2 = (380 \pm 50)$ μs. The good correspondence between these two values shows that the dispersion in $T_{1\rho}$ is essentially due to intermolecular interactions.

Between ~0°C and the highest temperature studied (~90°C) exchange between phase a and phase b comes into play so that measured values of $T'_{1\rho a}$ and $T'_{1\rho b}$ are no longer the intrinsic relaxation times of the respective phases. Relaxation in this temperature range is denoted[10] as being in the 'intermediate exchange regime'. This is a transition region between the slow exchange region and the 'fast exchange region' in which the observed relaxation rate is the sum of the intrinsic rates of each phase weighted according to their size fractions[10]. The fast exchange regime could not be investigated since in this sample it starts at a temperature exceeding the boiling point of water (see *Figure 1* and ref. 10).

Figure 4 shows a plot of $1/T'_{1\rho a}$ vs. H_1 at $T = 25$°C (i.e. in the intermediate exchange regime). The same data plotted as a function of $\omega_1^{1/2}$ does not yield a straight line indicating that intermolecular interactions are no longer predominant. In principle the data can be described using

equation (1). This requires knowledge of the parameters $T_{1\rho a}$, $T_{1\rho b}$, P_b and τ_b. $T_{1\rho a}$'s in the intermediate exchange region are found by projecting the $T'_{1\rho a}$ (or $T_{1\rho a}$) values of the slow exchange region to higher temperatures (broken line in *Figure 1*). In this way we find that $T_{1\rho a} = (25 \pm 5)$ ms at 25°C (*Table 1*).

In addition, it is necessary to determine to what extent translational motion in phase a at 25°C is expected to contribute to the $1/T'_{1\rho a}$ dispersion shown in *Figure 4*. The dotted line in *Figure 3* shows the expected $1/T_{1\rho a}$ dependence on $\omega_1^{1/2}$ at 25°C as calculated using equation (2). For this calculation values of D and T_{2a} at −40°C were used to obtain the corresponding values at 25°C assuming that both follow Arrhenius behaviour with $E_a = 7.4$ kcal mol^{-1}. Clearly, intermolecular interactions in phase a do not contribute to any appreciable extent to the $1/T'_{1\rho a}$ dispersion at 25°C (compare dotted line in *Figure 3* with data in *Figure 4*).

Evaluation of $T_{1\rho b}$ requires a model for molecular dynamics in phase b. To this end we utilize a model successfully used by Resing[15,16] in the analysis of rotating frame relaxation results of water adsorbed onto surfaces. In this model the phase b protons in the slow and intermediate exchange regions are in the rigid lattice regime. The onset of fast exchange corresponds approximately with the onset of motional narrowing behaviour in phase b. This means that at 25°C water molecules in phase b are irrotationally bound to the cellulose molecules (see *Figure 1*). It is assumed that at this temperature the correlation time of phase b protons is greater than T_{2b} and that a major change in dipolar energy of these protons occurs only if a nucleus jumps out of phase b. The time between such jumps is τ_b. The strong collision limit[17] is expected to apply to these phase b protons. Therefore, the theory developed[17] by Slichter and Ailion for the study of ultraslow motion can be utilized here. Then, $1/T_{1\rho b}$ due to such jumps out of phase b is given[17] by

$$\frac{1}{T_{1\rho b}} = \frac{1}{\tau_b} \frac{H_L^2}{H_1^2 + H_L^2} \tag{3}$$

where H_L is the local field in the rotating frame for the phase b protons.

Two comments regarding the validity of equation (3) are in order. Strictly speaking equation (3) applies to the case in which $H_L \sim H_1$. For $H_1 \gg H_L$ it can be shown[17] that the rate becomes 3/4 of that indicated by equation (3). However, for $H_1 \gg H_L$ the contribution made by $1/T_{1\rho b}$ to the observed relaxation rate of phase a is expected to be relatively small. Therefore use of equation (3) for all H_1 should not lead to serious errors in this application. In addition, in using equation (3) for $1/T_{1\rho b}$ it has been assumed that any contributions to this rate other than that due to diffusion out of phase b are negligible. A more detailed model which takes such a contribution explicitly into account is not warranted at the present stage of this research. A possible consequence of its neglect will be commented upon below. It should be emphasized that in spite of the above simplification in equation (3) it yields reasonable estimates for H_L.

Using equation (3), the condition of detailed balance, and the fact that $P_b \ll P_a$, we rewrite equation (1) as follows

$$\frac{1}{T'_{1\rho a}} = A + \frac{1}{\tau_a} \frac{H_L^2}{H_1^2 + 2H_L^2} \tag{4}$$

where $A = 1/T_{1\rho a}$ + other frequency independent contributions. The solid line in *Figure 4* was calculated from equation (4) using a least-squares curve fitting routine[18]. The adjustable parameters A, τ_a and H_L which produced the best fit are shown in *Table 1*. The value of A (*Table 1*) is approximately twice the value of $1/T_{1\rho a} = 40$ s^{-1} obtained at 25°C from *Figure 1*. This may be the result of (a) $1/T_{1\rho b}$ also containing non-jump terms and (b) the addition of a contribution from the exchange process itself. Such terms, by being neglected explicitly, could make the term A, obtained through the application of equation (4), appear larger than $1/T_{1\rho a}$. Although the present data (*Figure 4*) does not permit a more detailed investigation of such terms, the above discrepancy does point out their possible presence.

For the phase b protons $H_L = 1.7$ G (*Table 1*). This value is several times the expected local field for hydroxyl protons ($H_L \lesssim 0.5$ G). Since the exchanging species in this sample can only be cellulosic hydroxyl protons or water molecule protons, the assumption made earlier that water protons exchange between phases is justified.

The local field for protons of an irrotationally bound water molecule is ~3 G (see ref. 16). The fact that H_L of the phase b protons is only slightly larger than 1/2 this value indicates that these protons are not irrotationally bound. However, at first glance this would be contradictory to the above interpretation that the system at 25°C is in the intermediate exchange regime (see ref. 10 and *Figure 1*). In view of this apparent discrepancy we propose the following model for the dynamics of phase b protons. In order to satisfy the requirement for intermediate exchange the water molecule must be located at a cellulose binding site for a time greater than the T_2 of the phase b protons. However, while at such a site, the molecule is free to rotate sufficiently rapidly such that the proton local field becomes somewhat less than its rigid lattice value. In other words the translational and rotational motions of the water molecule are essentially uncoupled. Considering the possible hydrogen bonds that can form between a water molecule and a cellulosic OH group, this model is quite reasonable. It may be noted that the relatively fast rotation can also produce a frequency independent contribution to $1/T_{1\rho b}$. This would be consistent with a suggestion made earlier in the discussion of the magnitude of $1/T_{1\rho a}$ relative to the term A (*Table 1*).

Table 1 Summary of rotating frame relaxation results in cellulose–water samples at 25°C

MC (%)	*A*	$1/T_{1\rho a}$	$1/T_{1\rho ac}$	$1/T_{1\rho c}$	τ_a	τ_{ac}	H_L (G)
20.5	86±4	40±8			0.87±0.02		1.7±0.1
49.9			30±2	<3		1.7±0.1	1.3±0.1
218			10±1	<3		16±2	1.5±0.2

Rates and lifetimes are in s^{-1} and ms, respectively

Wet cellulose samples with MC > FSP

From the foregoing discussion it is apparent that the water molecules in phase b are in relatively close association with the cellulose (tightly bonded) whereas the phase a water molecules are somewhat more loosely bonded to the cellulose. The implication of this is that upon adding water to dry cellulose, the b-sites are filled first and then a-sites are filled[10]. Therefore any water added to the cellulose sample with $MC = 20.5\%$ is expected to occupy phase a binding sites.

Figure 1 shows the dependence of $T_{1\rho}$ at 6.7 Gauss on temperature for cellulose samples with $MC = 39\%$ and $MC = 200\%$. Both samples exhibit a sudden drop in $T_{1\rho}$ as the temperature is lowered below $-(12 \pm 2)$°C. This behaviour is common in macromolecule–water systems and represents a freezing phase transition. Since the water in phase a did not show such behaviour, we conclude that some of the water in these samples ($MC = 39\%$ and $MC = 200\%$) exists in a third phase c (phase b water molecules are too tightly bonded to cellulose to freeze at -12°C). The water in phase c is sufficiently free from the cellulose molecules so that it can freeze at -12°C. From the present data it is not possible to determine exactly what hydration level must be exceeded before phase c sites fill. However, it stands to reason that such a hydration level is closely related to the *FSP*.

It is interesting that for temperatures below -12°C, $T_{1\rho}$ values for the three samples are the same (*Figure 1*). This means that the rotating frame relaxation of the non-freezable water for samples with $MC \gtrsim 20\%$ does not depend on the exact value of the sample hydration level. This taken together with the fact that the sample with $MC = 20.5\%$ did not exhibit the freezing phase transition suggests that for each sample studied it is the phase a water which is observable below -12°C.

In order to gain further insight into the relaxation behaviour in samples with $MC > FSP$, values of $T_{1\rho}$ at 25°C were measured as a function of H_1 for samples with $MC = 49.9\%$ (*Figure 5*) and $MC = 218\%$ (*Figure 6*). Comparing these data to that of the sample with $MC = 20.5\%$ (*Figure 4*) it is apparent that qualitatively the behaviour of $1/T_{1\rho}$ with H_1 is very similar in each case. The data suggest that the major effect the addition of phase c water has, is to change the weighting of $1/T_{1\rho b}$ in the observed relaxation rate. This is consistent with the above discussion where it was pointed out that the phase c water is more like bulk water than that in phase a. In other words, $1/T_{1\rho a}$ is

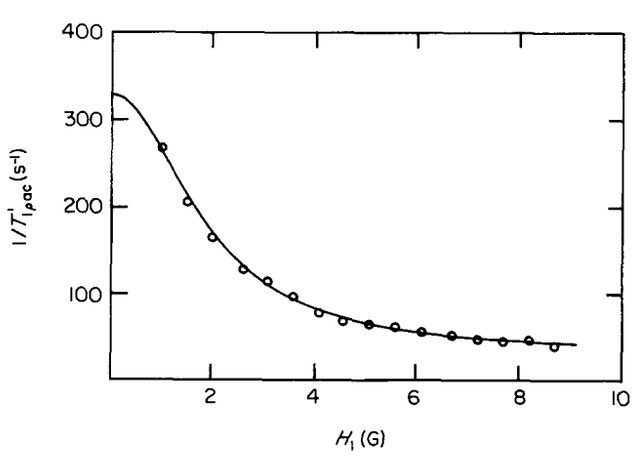

Figure 5 $1/T'_{1\rho ac}$ dispersion plot in hydrated cellulose at 25°C. $MC = 49.9\%$. The solid line is discussed in the text

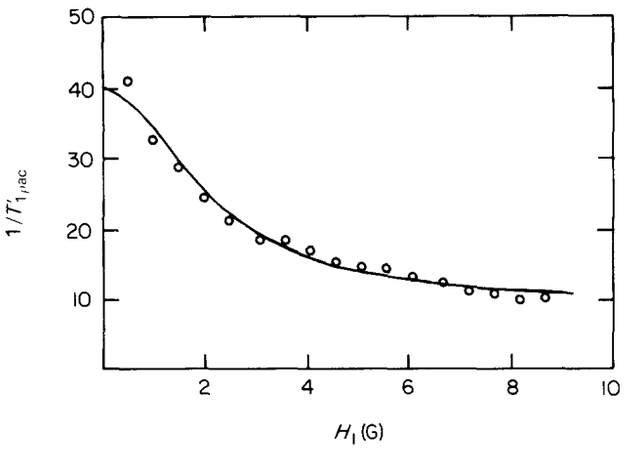

Figure 6 $1/T'_{1\rho ac}$ dispersion plot in hydrated cellulose at 25°C $MC = 218\%$. The solid line is discussed in the text

essentially independent of H_1, as is $1/T_{1\rho c}$, and any variation in the observed rate with H_1 in samples with $MC > FSP$ is due to $1/T_{1\rho b}$.

From the above discussions it is evident that $T_{2c} > T_{2a}$ so that all of the phase c water is observable at 25°C. In addition all $T_{1\rho}$ decay curves were exponential. As a consequence we conclude that at 25°C water molecules of phase c exchange rapidly (compared to $T_{1\rho a}$ and $T_{1\rho c}$) with those of phase a. Thus, for P_a, $P_c \gg P_b$, the effective rate ($1/T_{1\rho ac}$) of the combined phases a and c can be written

$$\frac{1}{T_{1\rho ac}} = P_a A + \frac{(1 - P_a)}{T_{1\rho c}} \tag{5}$$

The observed rate ($1/T'_{1\rho ac}$) in samples with $MC > FSP$ is then given by equation (4) where $1/T'_{1\rho a}$, A and τ_a are replaced with $1/T'_{1\rho ac}$, $1/T_{1\rho ac}$ and τ_{ac}, respectively. The solid lines in *Figures 5* and *6* are values of $1/T'_{1\rho ac}$ calculated using the 'best fit parameters' $1/T_{1\rho ac}$, τ_{ac} and H_L given in *Table 1*. In each case a very reasonable fit was obtained. The values of H_L for the three samples (*Table 1*) are the same within the accuracy of the experiments (average $H_L = (1.5 \pm 0.2)$ G). This is consistent with the earlier suggestion that the dispersion of the observed rate is due to that of $1/T_{1\rho b}$.

Evaluation of $T_{1\rho c}$ from equation (5) requires values for A and P_a. A in the samples with $MC > FSP$ is taken to be the same as in the sample with $MC = 20.5\%$ (*Table 1*). In order to find P_a for the samples with $MC = 49.9\%$ and $MC = 218\%$ the minimum MC ($= FSP$) at which all a sites are filled must be known. As indicated earlier this value corresponds to the maximum MC for which no freezing phase transition occurs. Assuming that $T_{1\rho}$ for samples with $MC > FSP$ vary linearly with MC, the FSP can be estimated as follows. Values of $T_{1\rho ac}$, just above the freezing phase transition (say -10°C), are plotted as a function of MC. Then, the MC is found for which $T_{1\rho ac}$ equals $T_{1\rho a}$ (sample with $MC = 20.5\%$) at the same temperature. Applying this approach to the data (*Figure 1*) we find $FSP \approx 22\%$. This means that in the sample with $MC = 49.9\%$, for P_a, $P_c \gg P_b$, the value of P_a is $22/49.9\% = 0.48$. Similarly, P_a for the sample with $MC = 218\%$ was found to be 0.1. Substitution of these P_a's and the values of A and $1/T_{1\rho ac}$ (*Table 1*) into equation (5) shows that due to the propagation of errors no unique value of $1/T_{1\rho c}$ could be obtained. However, taking the uncertainties into account we can conclude that

$1/T_{1\rho c} < 3\ s^{-1}$ (*Table 1*). Therefore, the correlation time (of rotational and translation diffusion) for the phase c water molecule is no more than one order of magnitude larger than in the bulk liquid. In other words, the mobility of water in phase c is not unlike that in the bulk liquid.

CONCLUSIONS

Three different phases (a, b and c) of water adsorbed onto cellulose have been identified. At 25°C the nuclear exchange between the phases a and b is in the intermediate exchange regime whereas between phases a and c the fast exchange regime applies. The b phase consists of water molecules tightly bonded to the cellulose. However, the results suggest that these water molecules undergo a rotation about the hydrogen bond direction at a rate exceeding the inverse lifetime in phase b. Protons of water molecules in phase a are relaxed by an intermolecular process. The diffusive motion involved has a diffusion constant associated with it which is estimated at $\sim 10^{-8}\ cm^2\ s^{-1}$ at 25°C. Water in phase c exhibits a freezing phase transition at about −12°C. This observation taken together with the fact that these water molecules of hydration have slowed down only about tenfold compared to molecules in the bulk liquid suggests that the phase c water is not too different from the bulk liquid.

The fact that water in each of the three phases is influenced by the presence of the cellulose suggests that all water in the samples studied is bound. In a descriptive manner the water in phases b, a and c could be classified as tightly bound, bound and very loosely bound, respectively.

To elucidate the dynamics of water molecules in the various phases further, a study of proton and deuteron T_1 and T_2 in cellulose–water systems is in progress in this laboratory.

REFERENCES

1 Berendsen, H. J. C. 'Water, A Comprehensive Treatise', (Ed. F. Franks', Plenum Press, New York, 1975, pp. 293–330
2 Neal, J. L. and Goring, D. A. I. *J. Polym. Sci. C* 1969, **28**, 103
3 Carles, J. E. and Scallan, A. M. *J. Appl. Polym. Sci.* 1973, **17**, 1855
4 Child, T. F. *Polymer* 1972, **13**, 259
5 Hse, E., Vogt, G. J. and Bryant, R. G. *J. Colloid. Interface Sci.* 1979, **70**, 338
6 Nyström, B., Moseley, M. E., Brown, W. and Roots, J. *J. Appl. Polym. Sci.* 1981, **26**, 3385
7 MacKay, A. L., Bloom, M., Tepfer, M. and Taylor, I. E. P. *Biopolymers* 1982, **21**, 1521
8 Ailion, D. 'Advances in NMR', Vol. 5, (Ed. J. S. Waugh), Academic Press, New York, 1971, p. 177
9 Woessner, D. E. and Zimmerman, J. R. *J. Phys. Chem.* 1963, **67**, 1590
10 Resing, H. A. *Adv. Mol. Relax. Proc.* 1967–68, **1**, 109
11 Wallace, J. C. and Peemoeller, H., unpublished
12 Burnett, L. J. and Harmon, J. F. *J. Chem. Phys.* 1972, **57**, 1293
13 Zipp, A., Kuntz, I. D. and James, T. L. *J. Magn. Reson.* 1976, **24**, 411
14 Finch, E. and Schneider, A. S. *Biochim. Biophys. Acta* 1975, **406**, 146
15 Reising, H. A. *Adv. Mol. Relax. Proc.* 1972, **3**, 199
16 Resing, H. A., Foster, K. R. and Garroway, A. N. 'Magnetic Resonance in Colloid and Interface Sci—ACS Symposium Series', Vol. 34 (Eds. H. A. Resing and C. G. Wade), American Chemical Society, Washington DC, 1976, p. 516
17 Slichter, C. P. and Ailion, D. *Phys. Rev.* 1964, **135**, 1099
18 Bevington, P. R. 'Data Reduction and Error Analysis for the Physical Sciences', McGraw-Hill, New York, 1969, pp. 204–242