

DEUTERIUM NMR AND WATER ADSORPTION STUDIES OF THE EFFECT OF BEATING ON THE WATER-CELLULOSE INTERACTION

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Abstract

The interaction between water and cellulose has been studied by deuterium NMR and water sorption isotherm measurements for a bleached kraft pulp and an unbleached linerboard pulp beaten to various degrees. Measurements of 2H quadrupole splittings, spin-lattice relaxation rates and half height line widths have been carried out at different relative humidities. Furthermore, the spin-lattice relaxation rates at 86% relative humidity were measured in the frequency range 2-62 MHz for the bleached kraft pulp, unbleached linerboard pulp and for a microfibrillated cellulose sample. The relaxation rates show a strong dependence on the resonance frequency. The reorientation of the water molecules adsorbed on fibers can be described by two correlation times of the order of 10 ns and 50 ps respectively. Analysis of the experimental data does not show any effects of beating on the cellulose water interaction strength. All observations made can be explained by morphological changes of the fibers.

INTRODUCTION

The mechanical treatment of cellulose fibers in an aqueous environment, beating, improves many properties such as tensile strength, resistance to burst, smoothness of the exposed surface and flexibility of the sheets made from the treated fibers. In seeking for an explanation of these improved properties an understanding of the water-cellulose interaction could be of fundamental importance [1-3]. Our aim has been to investigate the possible influence of beating on this interaction. The various aspects of the beating process have been discussed in review articles [3-5] and this discussion will not be repeated here. We have used deuterium NMR spectroscopy for our purpose since deuterium NMR is a powerful technique for the study of the dynamics and ordering of liquid molecules in the vicinity of a solid interface. Water sorption isotherms have also been investigated for the variously beaten fibers.

For the deuterium nucleus with a spin $I = 1$, the quadrupole splittings give a direct measure of the orientational order parameter for adsorbed water molecules. The NMR relaxation rates are determined by molecular kinetic and structural parameters, and can be used to investigate the molecular dynamics of the adsorbed molecules. For the water molecule there are three nuclei 1H , 2H and ^{17}O that can be used for NMR spectroscopy. We have chosen 2H since it is experimentally more accessible than ^{17}O which for the water content used in this work gives NMR spectra that are too broad to be observed [6]. The cross-relaxation involving non-water protons [7-8] which can severely complicate the interpretation of the 1H NMR relaxation data is unimportant for 2H .

There has been a fair number of studies of cellulose-water interaction by both proton [9-12] and deuterium NMR [6, 13-16]. These studies have given information on the amount of bound water and the dynamics of the water adsorbed on cellulose fibres.

Progress in the theoretical interpretation of NMR data in heterogeneous systems has been rather slow and this might be attributed to the complexity of the structure of these systems. For example, the calculation of absolute proton relaxation times requires a detailed knowledge of the magnetic architecture of the system together with an insight in the molecular dynamics. Except in rather well-defined systems, this is intractable. Current interpretations have generally been based upon a two site exchange model, in which water is considered to be either free or associated in some way with the solid surface. Exchange between the bound and free phase is normally rapid on the NMR time scale which is of the order of the inverse of the residual interaction (typically in the millisecond range), and averaged molecular properties are detected. Although the amount of bound water is limited, the enhancement of the bound water intrinsic relaxation rate causes a significant effect on the population weighted average relaxation rate.

The purpose of the present work was primarily to investigate the possible effect of the beating on water-cellulose interaction. This has been done by measuring and analysing the water adsorption isotherms for variously beaten pulps. Furthermore, the deuterium NMR relaxation has been investigated in a wide frequency range and the extracted dynamic parameters are compared for the different pulp samples. Recent studies on micelles [17-18], lipid vesicles [19] and lyotropic liquid crystals [20, 21] have shown that it is necessary to carry out the relaxation measurements over a wide frequency range to obtain reliable and detailed molecular dynamic information. We also present data on the quadrupole splittings at different relative humidities (RH) for different kinds of pulp beaten to various degrees.

EXPERIMENTAL

Sample Preparation

A never-dried bleached softwood kraft pulp (Imperial Anchor, Iggesund AB, Sweden) in Na^+ form was divided into three parts and subjected to different degrees of beating in a PFI mill. The pulp beaten to a certain degree was made into 80 g/m^2 sheets according to Scandinavian Standard SCAN-C 25:76. In order to exclude the effects of the fine material generated during the beating process, all the fines were removed in a Britt Dynamic Jar before sheet formation. The wet sheets were cut into $5 \times 20 \text{ mm}$ strips and soaked in D_2O for two days during which time the deuterium oxide was changed twice. The samples were equilibrated at room temperature at different RH using D_2O solutions saturated with different inorganic salts [22] for three months and the amount of D_2O adsorbed was determined by weighing.

A similar sample preparation procedure was also used for a never-dried unbleached linerboard pulp (SCA Nordliner Munksund, Sweden) with $\kappa = 103$. To shorten the time to reach equilibrium a small fan (1.2 W) was introduced into each dessicator. The fan was controlled by a timer. The unbleached linerboard pulp contained 14.6% lignin (Klason lignin). The carbohydrate analysis gave: arabinose 1.6%, xylose 9.8%, mannose 8.3%, galactose 1.7% and glucose 78.6%.

Microfibrillated cellulose (MFC) samples were also made into sheets by forming successive layers of very low grammage (10 g/m^2). A special wire with $10 \text{ }\mu\text{m}$ holes was used.

Water Sorption Isotherm Determinations

A quartz spring apparatus as described in reference [23] was used to determine the adsorption and desorption isotherms for the linerboard pulp subjected to different degrees of beating. The quartz springs were calibrated using standard weights before starting the experiment. For the desorption isotherm wet samples were exposed to atmospheres of progressively decreasing RH, *viz.*, 97, 86, 75, 66, 56, 49, 35, 31, and 11.5%. Inorganic salt solutions were used to control the humidities [22]. Equilibrium was attained within three days for low relative humidities while samples exposed to an atmosphere above 80% RH attained equilibrium after about one week. The dry pulp weight has been determined by drying over phosphorus pentoxide. To obtain the adsorption isotherms the dried cellulose samples were conditioned at progressively increasing relative humidities as given above.

NMR Measurements

The deuterium quadrupole splittings for the bleached kraft pulp samples and the unbleached linerboard pulp samples were measured on a Bruker MSL-90 Fourier-transform spectrometer equipped with an iron-core magnet and a 4.7 T superconducting magnet. For each sample a bundle of parallel pulp sheet strips was sealed in a 10 mm standard NMR tube and the sample was arranged in such a way that the sheet plane was perpendicular to the magnetic field. The deuterium spectra were recorded using the quadrupole echo pulse sequence [24]. The half-height line widths were determined by fitting a gaussian function to the recorded spectra. The spin-lattice relaxation times T_{1Z} were measured by the inversion recovery method [25] at ten different frequencies; from 2 to 13.8 MHz using the Bruker MSL-90 spectrometer, at 30.7 MHz using the same spectrometer connected to the superconducting magnet, at 46 MHz on a Varian XL-300 spectrometer and at 61.4 MHz on Bruker AM-400 spectrometer. The relaxation times for the quadrupole order T_{1Q} were measured from

3 to 30.7 MHz with the phase cycled Jeener-Broekaert pulse sequence [26-28]. From the recovery curves for the magnetization the relaxation times T_{1Q} and T_{1Z} were extracted simultaneously by nonlinear curve fitting. T_{1Z} measured using the Jeener-Broekaert pulse sequence and the inversion-recovery method always agreed within experimental error. The temperature was controlled to $25 \pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

Water Adsorption and Desorption Isotherms

To further study the beating process we have measured the water sorption isotherms for the samples used in the NMR experiments. This is especially interesting since it has been proposed [29] that beating influences the water-cellulose interaction strength, which should show up in the isotherm. The water adsorption isotherm data for bleached kraft pulp are in good agreement with literature data [23, 30-32], only minor differences (less than 10%) are observed even for samples with rather large differences in the degree of beating. For the high yield unbleached liner-board pulp, as illustrated in Figure 1, there was for the extremely beaten pulp a significant increase in the water sorption.

The water sorption isotherms obtained have been analysed in terms of the BET equation [33] and the *Polanyi's* potential theory [34, 35]. The BET equation can only be fitted to the experimental isotherm data at low RH whereas the potential theory fits the experimental data almost perfectly. In the potential theory the interaction between the solid surface and adsorbate above that in the condensed liquid phase is assumed to be of the van der Waals type, so that the adsorption potential decreases with the inverse cube of the distance from the surface. i.e. the adsorption potential function is written

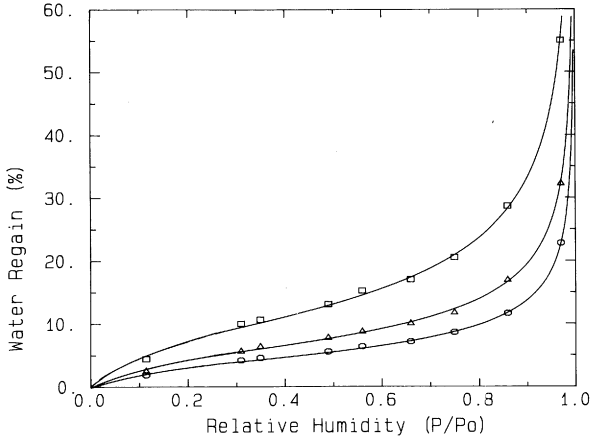


Figure 1: Water desorption isotherm for unbleached linerboard pulp samples beaten to various degrees. \circ , \triangle and \square represent respectively 500, 5000 and 25000 PFI beaten pulp. The line denotes the best fit of the potential theory to the experimental data.

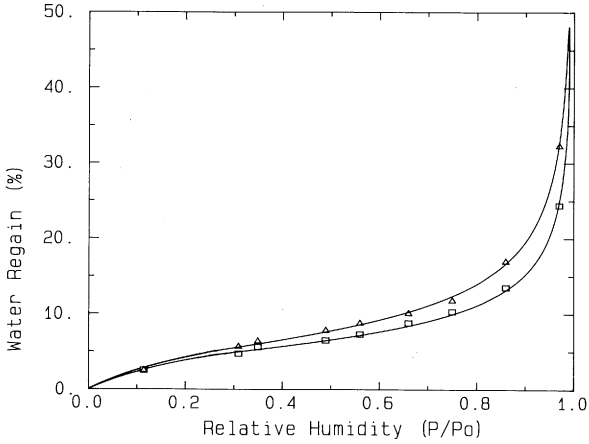


Figure 2: Water desorption (\triangle) and adsorption (\square) isotherms for unbleached linerboard pulp beaten to 5000 PFI.

$$\epsilon(x) = \frac{\epsilon_0}{(a+x)^3} \quad (1)$$

where a is the distance of closest approach of the order of one molecular radius and ϵ_0 is an interaction parameter. The potential at the distance x from the surface being just sufficient to cause adsorption is given by

$$\epsilon(x) = RT \ln\left(\frac{P_0}{P}\right) \quad (2)$$

By assuming that the amount adsorbed can be attributed entirely to a multilayer liquid film, the thickness x of the film is related to the adsorbed amount W per gram of pulp by

$$W = \rho A x \quad (3)$$

where A is the specific surface area of the solid surface and ρ is the density of the liquid. On combining equations eqs. (1)-(3) one obtains

$$W = -\alpha + \beta \left[\ln\left(\frac{P_0}{P}\right) \right]^{-\frac{1}{3}} \quad (4)$$

where α is defined as

$$\alpha = a A \rho \quad (5)$$

and β as

$$\beta = A \rho \left(\frac{\epsilon_0}{RT} \right)^{\frac{1}{3}} \quad (6)$$

The ratio

$$\frac{\alpha}{\beta} = a \left(\frac{\epsilon_0}{RT} \right)^{-\frac{1}{3}} \quad (7)$$

contains only the parameters a and ϵ_0 which determine the adsorption potential function $\epsilon(x)$. The α and β values computed by means of a nonlinear curve fitting of W versus $\frac{P}{P_0}$ for the unbleached linerboard kraft pulp samples are given in Table 1.

Sample	α	β	α/β	$\frac{\alpha_i}{\alpha_{500}}$
500 PFI	3.88	8.31	0.47	1.0
5000 PFI	5.67	11.9	0.48	1.46
25000 PF	9.71	20.2	0.48	2.50

Table 1: Potential adsorption theory parameters for the unbleached liner-board pulp beaten to various degrees.

As shown in Table 1, the samples subjected to different degrees of beating have the same $\frac{\alpha}{\beta}$ ratio within the error limit. The most reasonable explanation is that for the same type of pulp beating does not change the closest approach parameter a or the interaction parameter ϵ_0 . The differences in α and β for the samples subjected to different degrees of beating merely reflect the differences in the specific surface area \mathcal{A} . When the a and ϵ_0 parameters are constant, the ratio of α parameters between samples subjected to different degrees of beating gives a direct measure of the increase in the specific surface area caused by the beating

$$\frac{\alpha_i}{\alpha_{500}} = \mathcal{A}_i / \mathcal{A}_{500} \quad (8)$$

α_i is the α parameter for the 5000 PFI or 25000 PFI beaten pulp and α_{500} is the α parameter for the 500 PFI pulp. The water contact surface area of the extremely beaten pulp (25000 PFI) is 2.5 times of that of the slightly beaten one (500 PFI). Taking $\mathcal{A} = 200\text{m}^2/\text{g}$ (a typical value for cellulose fibers [37]) as the specific surface area for the 500 PFI beaten pulp, our estimation of the closest approach parameter a from α is 1.9 \AA which is very close to the water molecule radius (2.17 \AA estimated from the the area occupied by an adsorbed water molecule). Similarly, the calculated adsorption potential at the distance of closest approach is $\epsilon(0) = 22.0 \text{ kJ/mol}$ which is sizeable compared with RT as it must be in order to substantially lower the equilibrium pressure of water in accordance with eqs. (1) and (2). Furthermore, it is of a reasonable magnitude as compared with the estimated van der Waals interaction free energies [35, 36].

Sample	25000 PFI	5000 PFI	500 PFI	MFC
<i>Adsorption/desorption ratio</i>	0.83	0.84	0.84	0.84

Table 2: The average *adsorption/desorption* ratios over the range 35 to 86% RH for unbleached linerboard pulp beaten to various degrees and for the MFC sample.

Sorption hysteresis phenomena as illustrated in Figure 2 and Table 2 were observed for the linerboard pulp samples. The adsorption desorption ratios presented in the above table are average values over the range 35 to 86%RH. This ratio is almost constant in the whole hysteresis range for all the samples, which are in good agreement with the literature value 0.86 ± 0.02 for wood pulp fiber [37]. The explanation of sorption hysteresis of porous materials is by and large an unsolved problem in surface chemistry. In the case of cellulose fibers, Urquhart et al have done very extensive studies [38, 39] and given some interesting proposals about changes of the availability of the polar hydroxyl groups of the cellulose. However, the hysteresis effect exhibited for adsorption and desorption of water on cellulose fibers might as well be related to a wide distribution of pore sizes in combination with contact angle hysteresis.

^2H Quadrupole Splittings and Relaxation. Dependence on the Adsorbed Amount

Figure 3 shows the ^2H spectrum from D_2O adsorbed on pulp sheets that are oriented perpendicularly to the magnetic field. The spectrum shows a quadrupole doublet centered at the Larmor frequency.

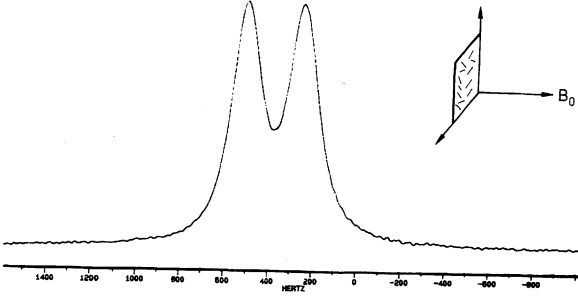


Figure 3: A typical 2H NMR spectrum for D_2O adsorbed on pulp sheets oriented perpendicularly to the magnetic field B_0 .

The magnitude of the quadrupole splitting gives information about the time average orientation of the adsorbed water molecules with respect to the magnetic field [40].

$$\Delta_Q = \frac{3}{4} | \chi (3 \overline{\cos^2 \theta_{ML}} - 1) | \quad (9)$$

Δ_Q is the frequency separation between the two lines in the spectrum. χ is the quadrupole coupling constant for 2H in the water molecule, which is a molecular quantity and we use the value $\chi = 213$ kHz [41]. θ_{ML} in eq. (9) is the time dependent angle between a O-D bond in an adsorbed water molecule and the laboratory fixed magnetic field B_0 and the bar indicates a time average. For water molecules adsorbed on cellulose fibrils that are fixed in a sheet eq. (9) can be rewritten using the addition theorem for spherical harmonics

$$\Delta_Q = \frac{3}{4} | \chi \frac{1}{2} (3 \overline{\cos^2 \theta_{MF}} - 1) (3 \cos^2 \theta_{FL} - 1) | \quad (10)$$

θ_{MF} is the time dependent angle between the water O-D bond and the local symmetry axis which in our case is the fibril axis. The fibrils in cellulose fibers are in general not parallel to the fiber axes and amorphous regions as well as lignin and hemicellulose are also present in our samples [42]. The extent of orientation of the fibrils is, however, sufficient to give rise to orientation effects in NMR. We make the approximation that for sheets oriented perpendicularly to the magnetic field $\theta_{FL} = 90^\circ$ for all fibrils and the observed quadrupole splitting is

$$\Delta_Q = \frac{3}{4} | \chi S_{MF} | \quad (11)$$

The order parameter S_{MF} describes the ordering of the water molecules relative to the fibril axis. A nonzero S_{MF} indicates that the D_2O molecules confined to the cellulose fibre interfacial region have lost a part of their reorientation freedom.

$$S_{MF} = \frac{1}{2} (3 \cos^2 \theta_{MF} - 1) \quad (12)$$

When the sheet is not oriented perpendicularly to the field or for a pulp sample a continuous distribution of fibre orientations relative to the magnetic field are present in the sample and the 2H NMR spectrum consists of a superposition of doublets with different quadrupole splittings according to eq. (10). In order to experimentally observe the 2H quadrupole splittings from D_2O adsorbed on cellulose it is necessary to use oriented sheets [16] or macroscopically oriented fibres [6].

The deuterium quadrupole splittings have been measured for a bleached kraft pulp and an unbleached linerboard pulp subjected to different degrees of beating and equilibrated at various RH. As can be seen in Figure 4 and 5 the splittings decrease with increasing relative humidity.

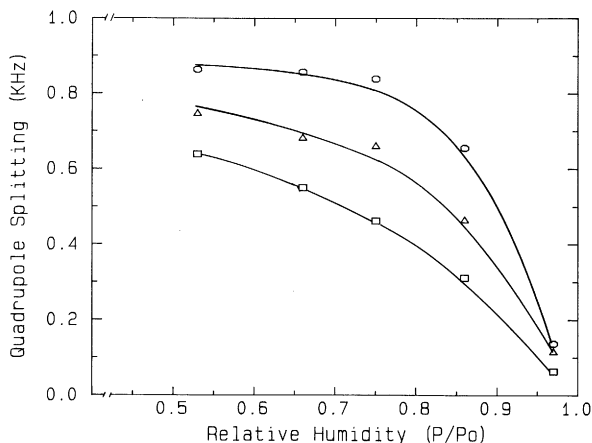


Figure 4: ^2H NMR quadrupole splittings for D_2O adsorbed on never dried bleached kraft softwood pulp beaten to various degrees (\circ : 500 PFI, \triangle : 5000 PFI and \square : 25000 PFI) as a function of RH.

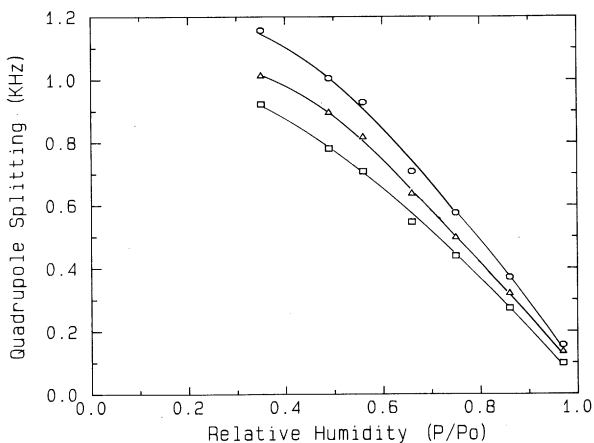


Figure 5: ^2H NMR quadrupole splittings for D_2O adsorbed on never dried unbleached linerboard pulp beaten to various degrees (\circ : 500 PFI, \triangle : 5000 PFI and \square : 25000 PFI) as a function of RH.

The lower RH used corresponds roughly to one monolayer of adsorbed water molecules whereas at higher moisture content multilayer adsorption occurs [30, 31, 43]. The water molecules in the outer layers have weaker interaction with the cellulose fiber surface because of the larger distance from the surface as described by the potential theory discussed above and have molecular motions that are more or less isotropic. Due to the fast exchange between the adsorbed water molecules in different sites and different layers the observed quadrupole splittings gives a population weighted average of the order parameter for the adsorbed D_2O molecules. The splitting decreases with increasing RH due to the increase of the less perturbed fraction. The observed quadrupole splitting is given by:

$$\Delta_{Q,obs} = \sum_i p_i \Delta_{Q,i} \quad (13)$$

where $\Delta_{Q,i}$ is the intrinsic quadrupole splitting at site "i" given by equation (11) and p_i is the probability that the nucleus resides in site "i". If the very simplified assumption is made that only two categories of water molecules are considered, *viz.*, D_2O molecules which have lost a part of its rotational freedom in the vicinity of the cellulose interface thus giving a nonvanishing average quadrupole splitting $\Delta_{Q,b}$ and D_2O molecules with a isotropic reorientation giving no contribution to the quadrupole splitting, the above equation can be simplified to:

$$\Delta_{Q,obs} = \Delta_{Q,b} p_b = \Delta_{Q,b} \frac{W_b}{W_w} = \Delta_{Q,b} K A \frac{W_{cell}}{W_w} \quad (14)$$

p_b is the fraction of D_2O molecules with average quadrupole splitting $\Delta_{Q,b}$ and W_b , W_{cell} and W_w represent respectively the weight of the D_2O with nonvanishing quadrupole splitting the weight of the dry cellulose fibers and the total weight of D_2O contained in the sample. K is a molecular constant related to molecular weight of water and cellulose. A similar equation can be obtained for the observed spin-lattice relaxation rates $R_{1,obs}$ and the half height line widths $\Delta\nu_{\frac{1}{2},obs}$

$$R_{1,obs} = R_{1,f} + (R_{1,b} - R_{1,f}) K A \frac{W_{cell}}{W_w} \quad (15)$$

$$\Delta\nu_{\frac{1}{2},obs} = \Delta\nu_{\frac{1}{2},f} + (\Delta\nu_{\frac{1}{2},b} - \Delta\nu_{\frac{1}{2},f}) K A \frac{W_{cell}}{W_w} \quad (16)$$

$R_{1,f}$ is the spin-lattice relaxation rate for the nonperturbed water fraction. The meaning of the other symbols in these equations are analogous. According to the above equations ΔQ_{obs} , $R_{1,obs}$ and $\Delta\nu_{\frac{1}{2},obs}$ versus $\frac{W_{cell}}{W_w}$ should give straight lines with slopes proportional to the specific surface area \mathcal{A} . Ratios of the slopes between samples subjected to different degrees of beating are equal to the corresponding specific surface area ratios. Such plots are given in Figure 6-8 for the unbleached linerboard pulp equilibrated at different RH. They are practically straight lines except at low RH where the isotropic water fraction disappears. The slope ratios for the linear part are presented in Table 3

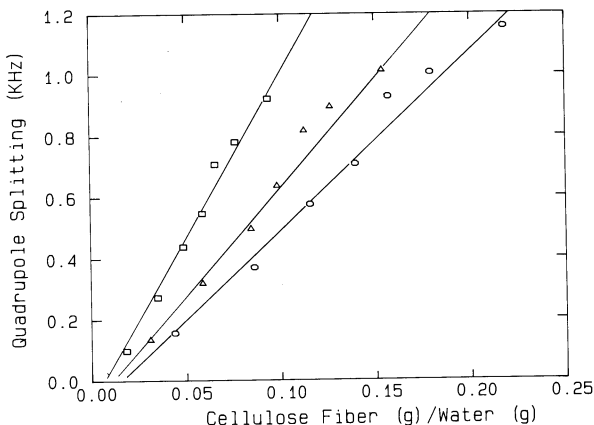


Figure 6: 2H quadrupole splittings for D_2O adsorbed on unbleached linerboard pulp beaten to various degrees (○: 500 PFI, △: 5000 PFI and □: 25000 PFI) as a function of the $\frac{W_{cell}}{W_w}$ ratio.

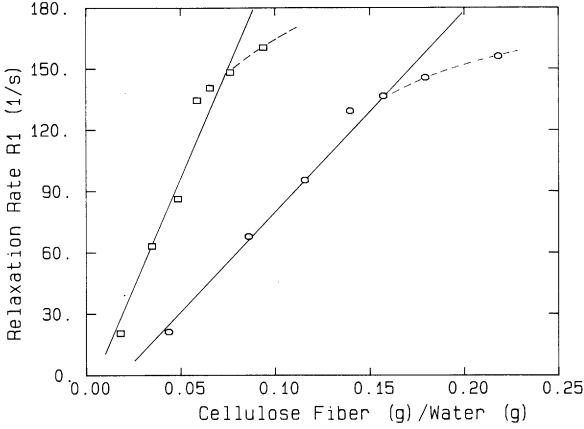


Figure 7: 2H spin-lattice relaxation rate R_1 for D_2O adsorbed on unbleached linerboard pulp beaten to two different degrees (\circ : 500 PFI, \square : 25000 PFI) as a function of the $\frac{W_{cell}}{W_w}$ ratio.

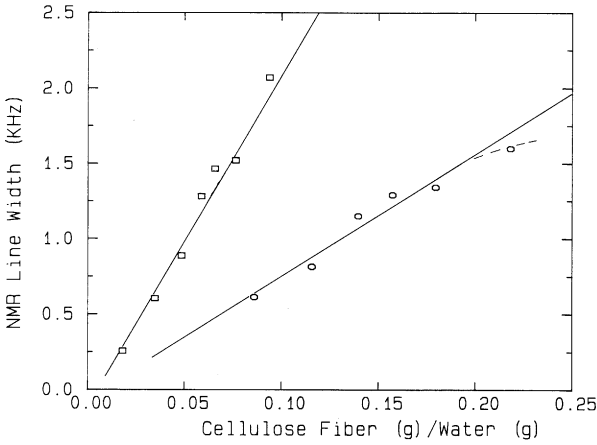


Figure 8: The half height line widths for unbleached linerboard pulp beaten to two different degrees (\circ : 500 PFI, \square : 25000 PFI) as a function of the $\frac{W_{cell}}{W_w}$ ratio.

Sample	Δ_Q data	R_1 data	$\Delta\nu_{\frac{1}{2}}$ data	Isotherm data
500 PFI	1.0	1.0	1.0	1.0
5000 PFI	1.33			1.46
25000 PFI	2.3	2.4	2.4	2.50

Table 3: The specific surface area ratio A_i/A_{500} calculated from the quadrupole splitting, spin-lattice relaxation rate, half height line width and isotherm data for unbleached linerboard pulp beaten to various degrees.

The results obtained from NMR experiments are very close to those deduced from the isotherm experiment in the previous subsection. This again indicates that for the high yield unbleached linerboard pulp the main effect of beating on individual fibers is to increase the specific surface. It should be realized that the new surface area created during the beating should not necessarily influence the measured quadrupole splitting at a given RH. If the new surface has the same properties as the existing surface and the relative amounts of water in the different layers are not affected, the quadrupole splitting should stay constant. The beating process is accompanied by external and internal fibrillation [3-5]. Internal fibrillation implies that fibrils inside the fibres are being loosened which results in disrupted and less well oriented fibril layers and increased fiber swelling and plasticity. The internal fibrillation is especially interesting to us since it is primarily the D_2O associated with the fibrils in the S_2 -layer that gives rise to the observed quadrupole splittings. This disorganization of the fibre structure can obviously contribute to the more effective averaging of the quadrupole order for the D_2O adsorbed on beaten pulp. This could be the reason why the specific surface area ratios obtained from the NMR experiment are slightly smaller than the results deduced from the sorption isotherm. It also explains the slight decrease of quadrupole splitting for the bleached kraft pulp samples without corresponding increase of the adsorbed amount [16]. Our 2H NMR quadrupole splitting data are consistent with the established picture of the beating operation [3-5, 44-47]. If the water-cellulose interaction strength increased by beating the motions of the water molecules should be more restricted and an increased

intrinsic quadrupole splitting would be expected. This is, however, not observed.

From our deuterium quadrupole splitting experiment we can thus not observe any influence of beating on the water-cellulose interaction strength for the unbleached linerboard pulp or for the bleached softwood kraft pulp. The changes in the spectra observed can be explained by changes in the morphology of the fibers.

Spin-lattice Relaxation Rate. Dependence on Resonance Frequency

In Figure 9 the ^2H spin-lattice relaxation rates $\frac{1}{T_{1Z}}$ for D_2O adsorbed on sheets of MFC, unbleached linerboard pulp and bleached kraft pulp equilibrated at 86% RH are given as function of resonance frequency ω_0 .

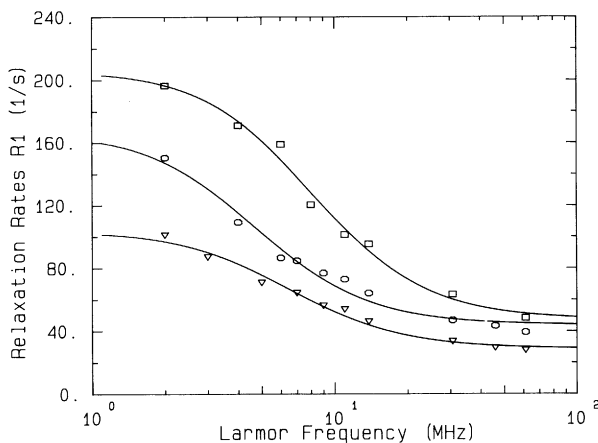


Figure 9: ^2H spin-lattice relaxation rate $\frac{1}{T_{1Z}}$ for D_2O adsorbed on MFC (∇), bleached kraft pulp beaten to 5000 PFI (\circ) and unbleached linerboard pulp beaten to 25000 PFI (\square) equilibrated at 86% RH. The lines show the best fits of the two-step model to the experimental data.

As seen, the relaxation rates are frequency dependent. This immediately shows that the extreme narrowing condition is not met and that molecular motions with frequencies lower than or in the range of the resonance frequency are present in the system. The general equation which describes the spin-lattice relaxation behaviour is [25]

$$\frac{1}{T_{1Z}} = \frac{3\pi^2}{20} \chi^2 [J_1(\omega_0) + 4J_2(2\omega_0)] \quad (17)$$

The spectral density functions $J_m(\omega)$ characterize the frequency distribution of the random molecular motions of the adsorbed water molecules. The main parameter in the spectral density function is the correlation time τ . Loosely speaking, the correlation time is the time a water molecule "remembers" its orientation with respect to the magnetic field.

Our experimental relaxation data can not be fitted to a simple isotropic reorientation model using a single correlation time. The water-cellulose interactions are inherently anisotropic on a time scale that is long compared to the reorientation time of the absorbed water molecule. The averaging of the quadrupole interaction is therefore most conveniently treated as a two-step process as has been done in other heterogenous systems [6, 16-21, 40]. In the first step a fast, slightly anisotropic reorientation motion partially averages the quadrupole interaction from χ to χS where S is an order parameter defined in the same way as S_{MF} in eq. (12) but averaged only due to the fast molecular motions. In the second step the quadrupole interaction is further averaged to χS_{MF} by a slower processes that might be the translational diffusion of water molecules over the curved fibril surface. On the NMR time scale large angular oscillations of the cellulose molecules are extremely infrequent as MacKay et al [12] concluded from the measured 1H second moment. If the motions described above are independent of each other and the time scales well separated the spectral density function can be written

$$J(\omega) = (1 - S^2) \frac{2\tau_f}{1 + (\omega\tau_f)^2} + S^2 \frac{2\tau_s}{1 + (\omega\tau_s)^2} \quad (18)$$

τ_f and τ_s are the characteristic correlation times for the local fast reorientation and slow motion respectively. S is the intermediate order parameter introduced above which quantify the average orientation of the water

molecule at the microfibril surfaces. According to eq. (18), the spectral density has a frequency dependence as shown in Figure 10. As can be seen in Figure 9, our experimental data are in good agreement with the "two-step" model, and in the studied frequency range it is sufficient to characterize the molecular motion for D_2O adsorbed on cellulose fibers by the two correlation times τ_f and τ_s . The fast correlation time τ_f and the slow correlation time τ_s obtained by the fit to the relaxation data are given in Table 4.

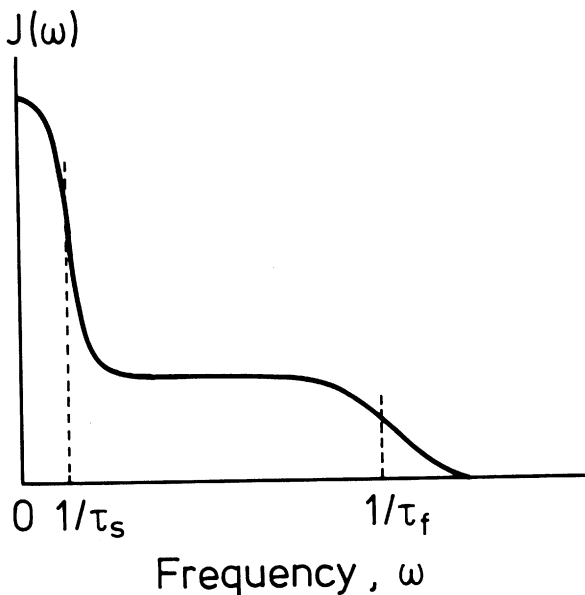


Figure 10: Spectral density function according to the "two-step" model illustrating the frequency distribution due to the slow and rapid motion of the adsorbed water molecules.

Sample	S	τ_s	τ_f
MFC	0.090	14 ns	43 ps
5000 PFI bleached	0.089	18 ns	56 ps
500 PFI bleached	0.082	33 ns	71 ps
25000 PFI unbleached	0.145	11 ns	73 ps
500 PFI unbleached	0.146	11 ns	76 ps

Table 4: The order parameter and correlation times obtained from the best fit of the two-step model to the experimental relaxation data for different samples at 86% RH.

The correlation time τ_f for the local, slightly anisotropic, reorientation motion of the adsorbed water molecules is slowed down by a factor of ~ 20 relative to bulk water ($\tau_{rot} = 2.4 \text{ ps}$ for pure water at 27°C [48]). The slow correlation time τ_s of the order of 10^{-8}s probably corresponds to the time for water molecule to diffuse along the curved surfaces of the microfibrils.

τ_f is the parameter that should be most directly related to the interaction between the cellulose fibers and water molecules. As can be seen there are only slight changes in this parameter between different types of pulp fibers. If there is any change with beating it is in the direction of faster reorientation for the water molecules on the beaten fibers. The slow reorientation time τ_s should be correlated to the morphology of the fibers. The bleached slightly beaten fibers should have the least delaminated structure and also give the longest time for diffusion around the fibrils. For unbleached linerboard pulp fibers there is not much change in τ_s with beating. This means that already the unbeaten fibers are enough swollen, having many dissociated carboxyl groups, to give a short τ_s . The higher S -values for unbleached fibers might be due to an interaction between the ionic groups and the adsorbed water molecules.

The fact that τ_s is shortest for MFC is easy to understand since this sample consists of separated fibrils. The short value of τ_f for MFC means

that even for this extremely beaten fibers it has not been possible to show an increase in the cellulose fiber-water interaction strength.

The spectral density function discussed above is formally defined as

$$J_m(\omega) = \int_{-\infty}^{+\infty} \overline{(F_m(t)F_m^*(t+\tau))} \exp(i\omega\tau) d\tau \quad (19)$$

where $\overline{F_m(t)F_m^*(t+\tau)}$ is the autocorrelation function of the second-order spherical harmonics $F_m(t)$ which describe the time-dependent orientation of the adsorbed water molecules. In the calculation made above to extract the correlation times from the T_{1Z} we have assumed that the $J_1(\omega_o)$ and the $J_2(\omega_o)$ are identical. This assumption can be tested by measuring the relaxation time T_{1Q} for the quadrupole order given by [26]

$$\frac{1}{T_{1Q}} = \frac{3\pi^2}{20} \chi^2 [3J_1(\omega_o)] \quad (20)$$

The measurement of T_{1Q} can be made by the Jeener-Broekaert pulse sequence [26-28]. Figure 11 shows a set of recovery curves from which both T_{1Z} and T_{1Q} can be extracted.

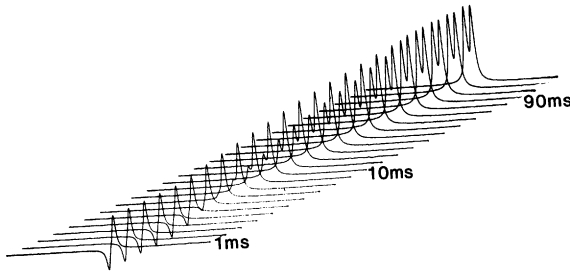


Figure 11: Recovery curves from the phase-cycled Jeener-Broekaert pulse sequence with quadrature detection for a MFC sample equilibrated at 86% RH.

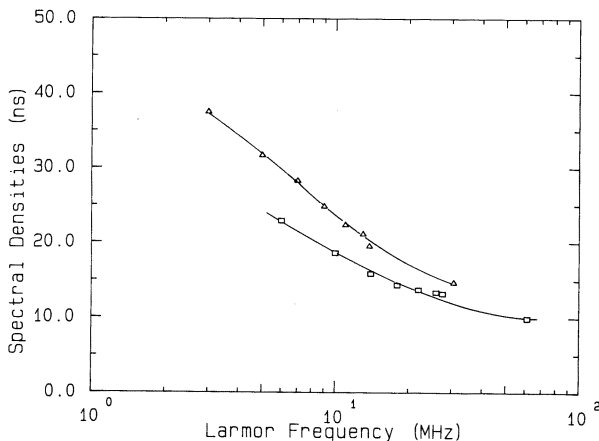


Figure 12: Spectral densities $J_1(\omega_0)$ (Δ) and $J_2(\omega_0)$ (\square) calculated from T_{1Q} and T_{1Z} at different resonance frequencies for D_2O adsorbed on MFC at 86% RH.

These measurement have been performed at a number of resonance frequencies. The deduced spectral densities are presented in Figure 12. The spectral densities $J_1(\omega_0)$ and $J_2(\omega_0)$ differ only slightly in the overlapping frequency range indicating that the assumption made is acceptable.

CONCLUSIONS

The 2H quadrupole splittings for D_2O adsorbed on various types of pulp sheet samples and the corresponding adsorption and desorption isotherms have been used to investigate the possible influence of beating on the water-cellulose interaction. 2H relaxation times for D_2O adsorbed on MFC and pulp sheets samples have been determined over a wide range of frequencies. Two correlation times which provide detailed molecular dynamic information for the adsorbed water molecules have been extracted. Due to the influence of the cellulose fibre surface, the

local water reorientation is anisotropic and slowed down by a factor ~ 20 as compared with bulk water. No effect of beating on the water-cellulose interaction strength parameters as probed by the NMR techniques and the water adsorption isotherms could be detected for the samples used. Hence, the predominant effect of beating found in these experiments are an increase of the specific surface area of the cellulose fiber.

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Transcription of Discussion

DEUTERIUM NMR AND WATER ADSORPTION STUDIES OF THE EFFECT OF BEATING ON THE WATER-CELLULOSE INTERACTION

L. Tie-Qiang, V. Henriksson, J. C. Eriksson and L. Odberg

M.J. Jaycock, Roe Lee Paper Chemicals

Looking at the isotherms you have got, the water absorption is on a low energy surface from the shape of the absorption isotherm. Although you have washed it to be free from particulate fines, you have not washed it free from hemicellulose. If we look at the thickness of the film as it increases with relative pressure, we would expect a situation where the hemicellulose in the absorbed water layer will become greater as the partial pressure increases. What about the explanation that the structural water you are looking at is primarily that bound to hemicellulose, if we distinguish hemicellulose from the fibre itself being the insoluble part of the wood pulp?

L. Odberg

We didn't observe any change in the E-parameter which is the energy interaction parameter. Of course, I am fully aware of the fibrils on the surface bound to the fibres which cannot be removed. We had expected more changes. We get the same correlation times, as in other hydrogen bonded systems. There is not a big difference for water molecules if they are bound to cellulose or hemicellulose molecules. The state of the water on the surface is not too different. We should not emphasise too much the state of hydrogen bonding between cellulose and water.

M.J. Jaycock

The control experiment required, if it could be done, was a saturated solution of hemicellulose in water. If the data obtained from that solution gave similar results to that which you had here, then you had strong evidence for it being in the hemicellulose involvement. If you had got different results then you had good reason for believing that your results were in fact interactions of water with the fibre.

K. Ebeling, James River Corporation

Have you tried to use the fines that the refining generates as the study material, and, if so, have you changed the particle size down to the crill dimensions? Does this have any effect on the energy parameter in your studies?

L. Odberg

Obviously, that is an experiment that we will do, but we have not as yet done so.

A. de Clercq, BASF

Do you differentiate with your method the water bound on the inner and outer surface of the fibres?

L. Odberg

No, this is the total amount, we cannot differentiate between the two. There is just between one and four mono-layers that we have been studying here. This is the amount of water there is on the fibres.

A. de Clercq

But this does include the inner surface?

L. Odberg

Yes, it does include the inner surface.

Prof. J. Silvy, Ecôle Française de Papeteries

In your paper, you say that using this method you need to use orientated sheets or macroscopically orientated fibres. Could you

make comments about the difficulty you have in preparing the samples?

L. Odberg

It is not really difficult. This has to do with NMR theory. You should have a definite orientation of your fibres in the magnetic field. If you have different orientations, you will have a superposition of spectra of the type shown in Fig. 3 of my paper.

As we all know, the alignment is not perfect as the fibrils in the fibre do not lie perfectly along the fibre axis.

Dr. J. Roberts, UMIST

Just to return to M. Jaycock's question regarding the hemicelluloses, can I ask if the micro-fibrillar cellulose is actually free of hemicellulose, and if so, whether you thought the difference in relaxation time is related to the absence of Xylans in the pulp? These are known to form crystalline hydrates with water, whereas cellulose of course cannot.

L. Odberg

We have washed the micro-fibrillated cellulose extensively and made it as free from hemicellulose as we can. Of course it does leak for a very long time. The change in re-orientation time was only from, say, 60 to 45 pico seconds. I do not think this is to be interpreted as too significant. It is, after all, a different material. The MFC comes from a sulphite pulp. The other samples come from kraft pulps. The sulphite pulp does have more charged groups. I did not have the isotherms for the MFC, so I would not try to interpret that difference in the NMR results.

J. Waterhouse, Institute of Paper Science, Atlanta

Are there any other non cellulosic systems where you see a change in the surface water interaction with your techniques?

L. Odberg

We have not studied any other materials than cellulosic fibres, but of course there are lots of investigations in the literature about, for example, water and proteins, etc. In general, one is getting away from the concept of firmly bound water around

hydrophillic surfaces. After all, the hydrogen bonding is the same as in water, why should it be bound much more strongly to a cellulose surface than to other water molecules?. My re-orientation times were only 20 times slower than in free water. Of course there is an interaction, but it is not much different to that in water.