

^1H NMR relaxation study of paper as a system of cellulose and water

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ANALYSIS BY NUCLEAR MAGNETIC resonance (NMR) techniques has provided information on both the macromolecular structure and the dynamics of cellulose (1, 2). High-resolution spectra of cellulose have allowed researchers to observe the fundamental polymorphism in cellulose and to characterize two different types of the native crystalline cellulose (3, 4). These results have been confirmed by electron diffraction experiments on micro-crystals, leading to partially resolved structures (5).

In cellulose samples of different origins, the proportions of crystalline polymorphs and other forms can be completely different. Moreover, amorphous fractions may be also present (6, 7). ^1H NMR relaxation techniques have been used to distinguish between crystalline and paracrystalline domains of cellulose microfibrils (8). Results are in agreement with the observation that a lower packing density characterizes paracrystalline cellulose domains.

In previous work, we characterized some important features of an antique paper dating back to the 15th century (7). We viewed the paper as a two-component material made of cellulose and water. Our analytical approach combined the techniques of pulsed low-resolution NMR, electron paramagnetic resonance (EPR) (9, 10), and ^{13}C CP-MAS (cross polarization-magnetic angle spinning). This approach allowed us to characterize some of the chemical

transformations that take place in the degradation of antique paper.

In our research work on the structure of recently made papers, we have focused mostly on the water-cellulose interactions, with attention to cellulose packing. We carried out experiments using pulsed ^1H NMR relaxation to study the bound water and free water in cellulose. Because paramagnetic impurities play a role in the NMR relaxation process, we also performed spectroscopy experiments using EPR.

EXPERIMENTAL PROCEDURES

Preparation of handsheets

The commercial pulps used to make the handsheets were bleached pine kraft pulp, cotton linters (or rag stock), and groundwood spruce pulp. Kraft and linters pulps were soaked in water and beaten in a Valley beater to Schopper-Riegler freenesses of 28°SR and 30°SR, respectively. Groundwood pulp, with a freeness of 55°SR, was used as received.

Handsheet papers were prepared with neutral sizing and with acidic rosin sizing. Commercial alkylketene dimer (AKD) was used in neutral sizing. The synthetic size was added to the fiber stock at pH 8.0 at 0.6% consistency (1.3% on o.d. pulp), with the pulp containing calcium carbonate filler (10% on a.d. pulp). Handsheets were prepared in the laboratory according to TAPPI Test Method T 205. These papers were air dried and heated for 10 min at 105°C.

For handsheets prepared with acidic sizing, commercial rosin size

ABSTRACT

The interaction between water and cellulose was studied in papers sized with neutral alkylketene dimer and in papers prepared with acidic rosin sizing. We analyzed samples using nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR). We measured molar ratios of cellulose/total water and cellulose/bound water. For linter and kraft acid papers, bound water is lower in acidic papers than in their neutral counterparts. The water content in groundwood paper is almost twice that of linter and kraft papers.

was added to the fiber suspension (2.5% on o.d. pulp). The pH was corrected to pH 5.0 using H_2SO_4 and alum. Kaolin was finally added (8.3% on o.d. pulp). Handsheets were prepared according to TAPPI T 205 and were air dried and heated for 10 min at 105°C.

The degree of sizing was measured according to the Cobb₆₀ test method (TAPPI T 441). For paper sized with AKD and those sized with rosin sizing, respectively, the results were:

- Kraft: 25.0 and 23.4 g/m²
- Linters: 30.0 and 28.0 g/m²
- Groundwood: 17.5 and 12.7 g/m².

Electron paramagnetic resonance

Electron paramagnetic resonance spectra were recorded at the X-band frequency (about 9.1 GHz) and at about 100 K, for a better signal-to-noise ratio, using a Varian E-9 spectrometer equipped with a standard variable temperature accessory. The field was measured with a Bruker BNM-20 gaussmeter, and the frequency was measured with a Sytron-Donner 6246A counter. All sam-

Temp., K	LINTERS		KRAFT		GROUNDWOOD		Ancient paper
	Neutral	Acidic	Neutral	Acidic	Neutral	Acidic	
293	1.55±0.05	1.30±0.04	1.25±0.04	1.14±0.03	1.07±0.03	1.25±0.03	0.60±0.02
283	1.15±0.03	1.00±0.03	0.80±0.03	0.60±0.03	0.70±0.02	0.83±0.03	0.46±0.02
263	0.65±0.03	0.63±0.03	0.42±0.02	0.50±0.05	0.34±0.02	0.40±0.03	0.28±0.02

1. T_2 spin-spin relaxation times for the slow relaxing component of water, milliseconds

ples were of comparable weight (about 30 mg). Sample heights were kept within 5 mm, so as to be well contained within the maximum sensitivity region of the instrument cavity.

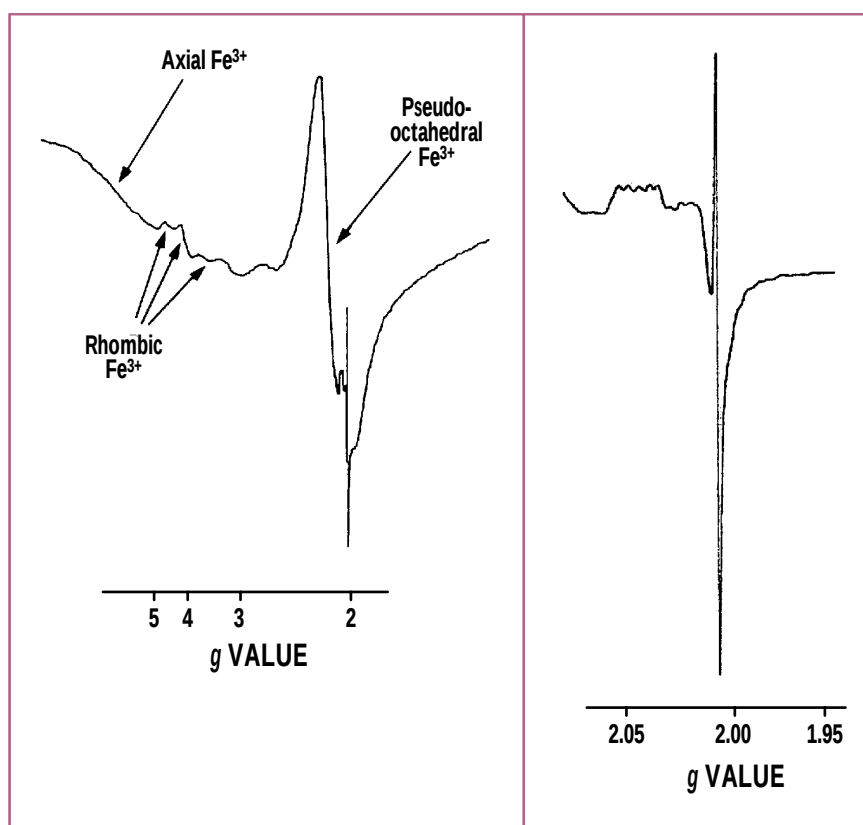
Ion concentrations were determined only in the case of rhombic iron by comparing the signal areas with appropriate calibration curves (10). Frozen solutions of $\text{Fe}(\text{C}_4\text{H}_6\text{N}_2)_3\text{Cl}_3$ (in which $\text{C}_4\text{H}_6\text{N}_2$ is 3-methylpyrazole) in acetonitrile were used for calibration (11). Measurements made with control samples indicated that the total error was below 10%.

Nuclear magnetic resonance

Samples of paper, stored at controlled conditions (23°C, 50% RH), were introduced into 5-mm NMR tubes, which were sealed. To keep the paper samples well within the NMR receiver coil, the height of each sample was approximately 0.5 cm. Each sample weighed 25.0 mg.

Free induction decays (FID) were acquired with a scan size of 2K words. The 90° pulse was 3.8 μs , and the dead time of the instrument was 8 μs . To get a good signal-to-noise ratio, we ran 16 scans.

Spin-lattice relaxation times, T_1 , in the full temperature range, were measured with the aperiodic saturation recovery sequence. This sequence consists of a long train of 90° pulses (15 in our case) spaced out in an aperiodic way (by decreasing the interval linearly). The last,

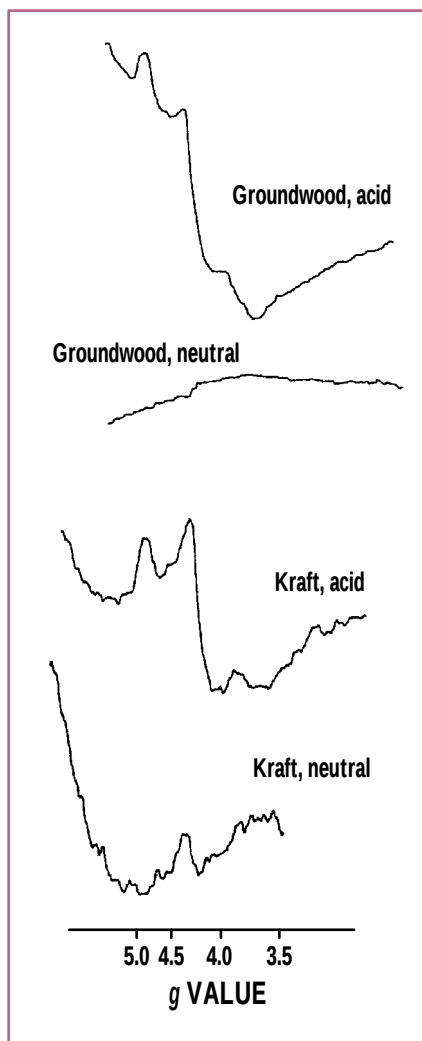


1. The low-temperature (110 K), X-band EPR spectrum of an acid-sized linters sample (left). On the right is a magnification of the sharp radical line at $g = 2.0035$.

smallest spacing between two 90° pulses in the pulse train was 0.2 ms. At the end of the pulse train, the relaxation recovery starts and proceeds through the usual delay t (12).

The aperiodic saturation recovery sequence was run according to a multiblock, multiscan procedure. In each experiment, we collected either 64 or 256 blocks, correspond-

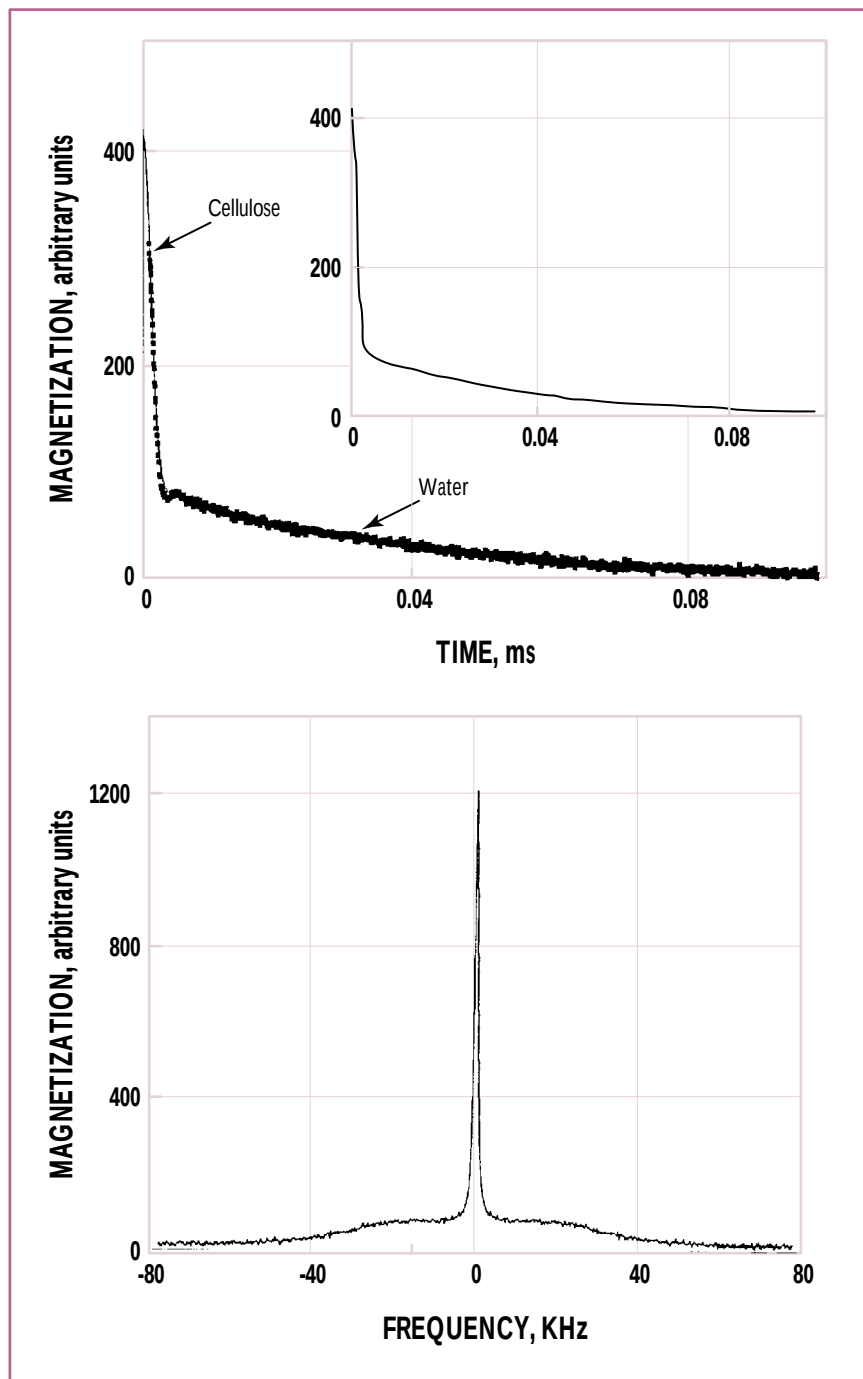
ing to 64 and 256 different delays. In the temperature range of 293–233 K, each block was acquired with a time domain corresponding to a word size of 512. At lower temperature, when bound water is frozen and its long decay is no longer observable, a scan size of 64 words was used, which was enough for recording the fast decay of the cellulose and of the



2. Detail of the $g = 4.3$ region of 110 K, X-band EPR spectra for samples of groundwood pulp and kraft paper. The large difference in rhombic Fe^{3+} content between the acid and neutral samples turns out clearly. The splitting of the signal into three absorptions indicates that the symmetry of iron slightly deviates from purely rhombic.

frozen water. To improve the signal-to-noise ratio, we allowed 16, 32, or 64 scans in the multiblock procedure.

The T_2 spin-spin measurements on the water component were carried out using a standard CPMG echo sequence, with $t/2 = 20 \mu\text{s}$. At least 512 echoes were collected (13). The



3. Free induction decay (top) and its Fourier-transformed spectrum (bottom) of an untreated paper sample. A fully simulated FID is shown in the insert (13). Its Fourier-transformed spectrum is shown in the lower graph. (Temp. = 293 K. Spectrometer frequency = 57 MHz).

relative amount of total water in each sample was measured with a standard high-resolution spectrometer operating at 200 MHz (Bruker

AC200), according to a procedure described previously (7), at 298 K. All measurements were performed from high to low temperature. When-

Temp., K	LINTERS		KRAFT		GROUNDWOOD ^a		Ancient paper ^b
	Neutral	Sizing	Neutral	Sizing	Neutral	Sizing	
293	0.92	0.90	1.1	1.0	1.68	1.65	0.93
283	0.92	0.82	1.0	0.8	1.60	1.65	0.93
263	0.84	0.68	0.85	0.67	1.42	1.44	0.85

^aLignin not included. See the experimental section.
^bSample 1 from Ref. 7.
 Errors are less than 5%.

II. Molar ratios of [water]/[cellulose] at different temperatures. The difference in ratios between high temperature and low temperature gives the amount of free water.

ever it was necessary to repeat a measurement, a fresh sample was prepared.

ANALYSIS OF NMR DATA

We obtained the molar ratio between water and cellulose by analyzing the free induction decays in the time domain (2K data points). The FID shape was fit using the proper function. This function is the sum of a gaussian function, corresponding to the cellulose decay, and an exponential function, corresponding to the water decay:

$$Y = C_0 + [W_{\text{cell}} \exp(-G_{\text{cell}} \cdot t^2)] + [W_{\text{water}} \exp(-E_{\text{water}} \cdot t)] \quad (1)$$

where

C_0 = mean value of experimental noise

W_{cell} = relative weight of the cellulose component

W_{water} = relative weight of the water component

G_{cell} = width of the gaussian decay

E_{water} = width of the exponential decay.

All of the parameters are obtained from a best fit of the FID.

Solving Eq. 2 yields the molar

ratio, MR , between water and cellulose:

$$MR = (W_{\text{water}}/n) / (W_{\text{cell}}/m) \quad (2)$$

where

n = 2, the number of protons in the water

m = 10, the number of protons in the monomeric unit of cellulose.

In groundwood pulp samples, a lignin content of 28% was subtracted from the total broad-band cellulose component. (We considered 10 protons to be a reasonable average per monomeric unit.) Since hemicelluloses in groundwood paper are mostly galactomannans, they have the same number of protons per monomeric unit of cellulose and do not need a separate treatment.

To calculate the relaxation times attributable to both the cellulose and the water, we treated the experimental data in the following way. In each block, resulting from the multi-block aperiodic saturation recovery sequence, we obtained the average value Y_i of the first 20 points of the decay. These points are the actual values of the magnetization in the

time range of 9–22 μs . In other words, Y_i has been reported as a function of the value of the current block.

Through a best-fit procedure (14), it is possible to obtain the relaxation times T_i of the cellulose, introducing these average data in the multi-exponential function:

$$Y_i = \sum W_i \exp(-t / T_{ii}) + C_0 \quad (3)$$

for $i = 1, \dots, k$, where k is the number of components. Here, W_i represents the relative weight for each component.

With the same function, it is possible to obtain the relaxation times attributable to the water. To obtain relaxation times of the water, we introduce the mean value Y_i of the points corresponding to the range 60–128 μs and apply a best-fit procedure again.

Cellulose and water have very different T_2 values. For the fast-relaxing cellulose component, T_2 is of the order of some tenth of a microsecond at room temperature. For the slowly relaxing water component, T_2 is of the order of 1 ms (Table I). As a result of these very different T_2 values, the cellulose component is fully decayed when the water component decay is measured. Therefore, under these conditions, it is possible to

obtain the $T_{1,i}$ values of the cellulose and the $T_{1,i}$ values of the water.

As shown in Table II, the ratio of free water to bound water has been obtained by direct comparison of the FIDs at 10°C and -10°C. In fact, at low temperature, free water is frozen, with a large line width corresponding to a short decaying FID, while bound water is still quite mobile.

RESULTS AND DISCUSSION

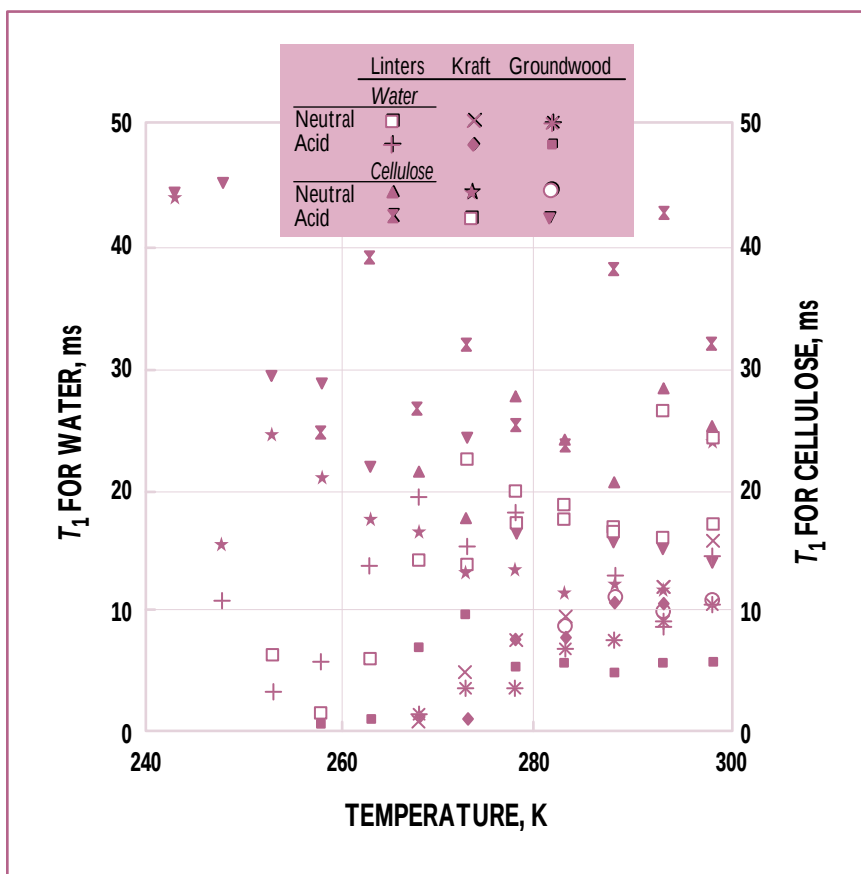
Study of EPR spectra

Figure 1 shows a representative EPR spectrum. The most evident characteristics are:

- A sharp radical line ($g = 2.0035$ and $\Delta w < 2$ gauss) of low and almost constant intensity
- An extremely broad signal (1400–1700 gauss) centered at $g \approx 6$, for which the intensity depends strongly on the sample. (The variable g is essentially the ratio between the frequency and the magnetic field at which the resonance occurs, while Δw is the line width expressed in gauss.)

Both of the above features were absent in the spectra of the antique paper made of rags. In the case of the groundwood pulp samples, the former signal at $g = 2.0035$ may be due to organic free radicals produced by the photolysis of lignin. Lignin is an aromatic polymer that can undergo different photochemical processes and produce phenoxyl radicals (15).

Degraded samples of groundwood pulp paper often show intense and complex spectral patterns. These patterns should give us insights on the aging process. The origins of the radical lines in the kraft and linters samples, which do not contain lignin, are more puzzling. Since cellulose cannot be responsible for these radicals, we tentatively assume that they derive from the bleaching



4. Data on fast relaxing components of T_1 for water and T_1 for cellulose vs. temperature. No correlation can be discerned between these fast relaxation components.

reagents used.

The broad signal at $g \approx 6$ is easily ascribed to high-spin Fe^{3+} in a strongly distorted field of axial symmetry. This signal is capable of giving rise to large zero field splitting parameters (16). Only transitions within the lowest Kramers' doublet are seen in this case, with a fictional spin 1/2 having $g_{\text{parallel}} = 2$ and $g_{\text{perpendicular}} = 6$, even though the real spin value remains 5/2 and the real g value remains 2.0.

The observed spectrum is the perpendicular part of the signal, whereas the parallel absorption is too weak and broad to be detected. Similar spectra, exhibited by well-defined metallo-organic or biological molecules, are generally much sharper, with widths of a few hundred gauss. This observation suggests

that the environment of iron in paper is much less defined and is spread over a wide interval of slightly different geometries. Furthermore, additional signals of variable but generally low intensity have been detected. These signals may be associated with traces of Mn^{2+} and small amounts of Fe^{3+} in quasi-octahedral ($g = 2.0$) or almost rhombic ($g \approx 4.3$) environments.

The most important paramagnetic impurity, Fe^{3+} , is present in these paper samples in three different stereochemical environments. One of these, the axial one, is dominant. However, while the amounts of both axial and octahedral iron are random and cannot be correlated with sizing or the type of paper, the rhombic species has been found almost exclusively in the acid-sized

samples. The spectra in Fig. 2 show the large difference in rhombic Fe^{3+} content between the acid and neutral samples for groundwood pulp and kraft papers. The experimental average concentrations are 100 ppm and 20 ppm, respectively, for the acid and neutral samples.

These paramagnetic impurities may act as strong relaxing agents. As a result, they may support the complex behavior of spin-lattice relaxation obtained by NMR (described below). In particular, rhombic iron at low temperature measurably shortens the T_1 relaxation of acid samples, in spite of its low concentration. Besides its efficiency as a spin relaxing agent, rhombic iron is also unique in favoring the hydrolytic degradation of cellulose (10). A possible rationale for these findings is that iron attains this particular stereochemistry by binding directly to the cellulose backbone.

^1H NMR relaxation study

As the upper graph of Fig. 3 shows, the free induction decay of a sheet of paper is marked by two distinct parts. The first part is a rapid decay attributed to the decay of cellulose. The second part is much slower and is attributed to the water (7, 17). From this FID, we obtain the Fourier-transformed NMR spectrum, which is as presented in the lower graph.

The experiment of Fig. 3 leads to several observations. First, it is possible to measure the ratio of water to cellulose. NMR software is available to assist. (We use a program called "STEFIT" as part of the software of SPINMASTER.) Second, because of the extreme difference in T_2 values, it is possible to perform relaxation measurements both for the water and for the cellulose component of the paper simply by choosing different time intervals (18). Third, the sharpness of the water signal can be used to define a "freezing point" for the water, or a parameter that gives information on the nature of hydro-

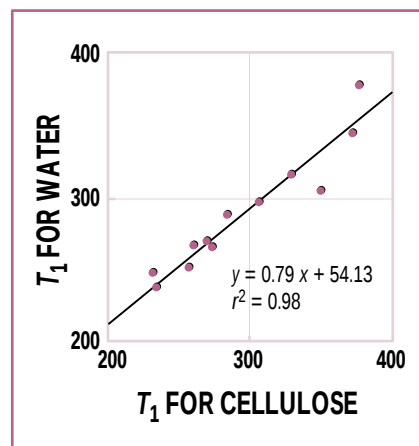
gen bonds between the water and the cellulose (17).

Moreover, the same method allows us to measure the molar ratio of cellulose to total water and that of cellulose to bound water. The ratio for total water can be obtained from the origin intercepts of the best fit curve that represents the full FID (insert in Fig. 3). To determine the ratio for bound water, we can apply the same method at a lower temperature (263 K). In this way, the bound water is measured by freezing the free water and measuring the signal of residual water. The same experiments might give information on porosity as a function of the temperature (19).

The sharpness of the water signal can also be used as a tool for analysis in the NMR imaging of any paper-containing material, such as a book or a document (20). A careful simulation of the FID experiments was performed on each sample, leading to the water/cellulose ratios shown in Table II. As the data show, the amount of water does not depend on the sizing. Instead, the ratio is a characteristic of the type of paper.

In ancient, well-preserved sheets of paper—paper of extreme high quality and made of rags—the amount of water is constant and identical to the amount observed in linters samples. This amount, including both free and bound water, corresponds to 0.9 molecules of water per glucose monomer. The amount of free water is almost negligible. In paper of inferior quality, the amount of total water is greater, which confirms that free water contributes to the total amount.

The T_1 measurements can be performed separately on cellulose signals and on water signals at room temperature. Table III lists data from measurements of the T_1 relaxation times attributed to the slow relaxation cellulose component. Remember, however, that for each type of

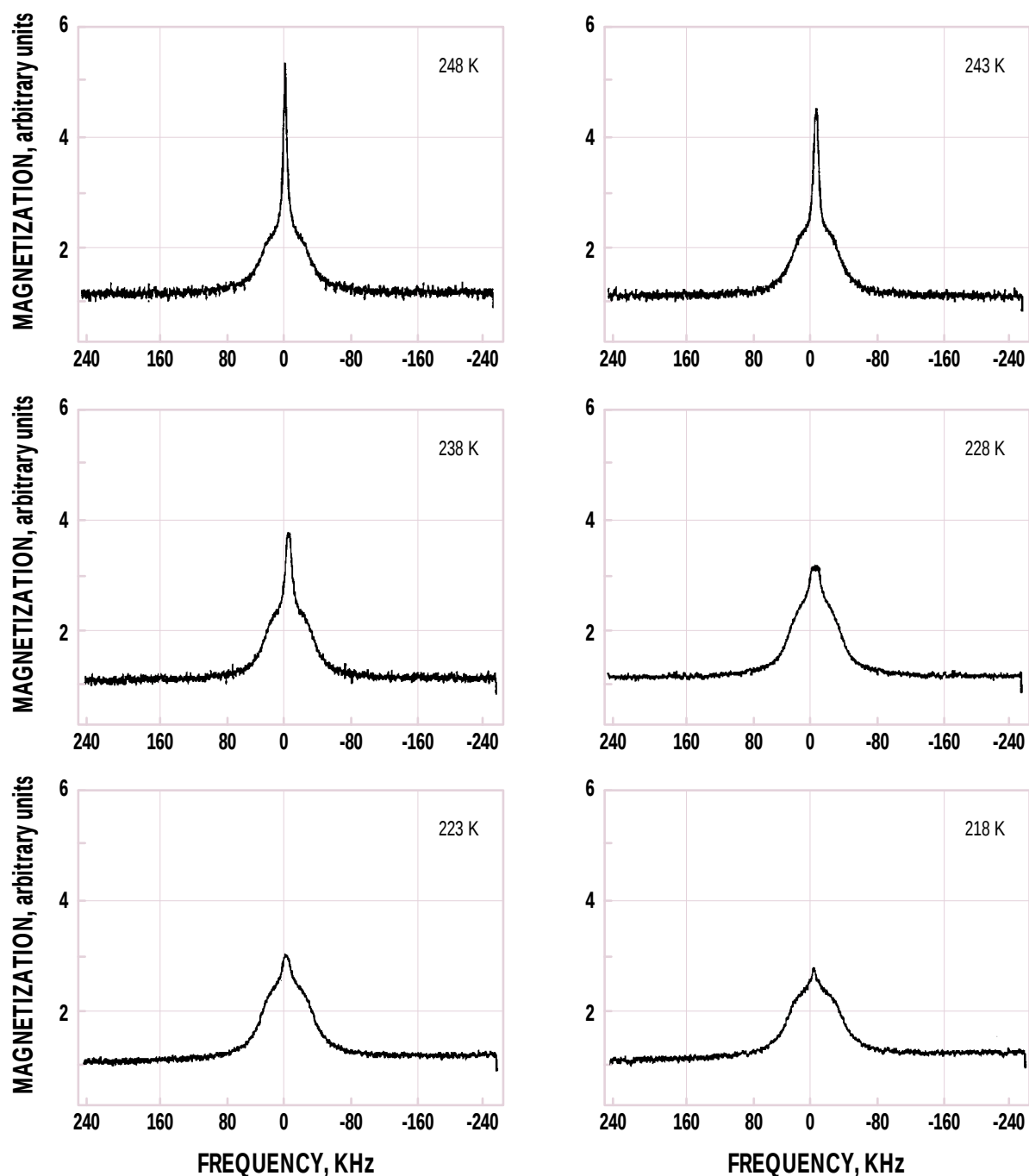


5. Slow relaxing components of T_1 for water and T_1 for cellulose in the range of 243–298 K. Data are relative to the linters sample with neutral sizing.

paper, there are two T_1 components. One component can be attributed to domains poor in paramagnetic impurities, accounting for 85–90% of the total magnetization. The other component can be attributed to domains rich in paramagnetic impurities, which would account for 10–15% of the total magnetization. This assignment derives from the observation that the short component of T_1 relaxation times does not seem to be related to the type of paper nor to its sizing. In support of this observation, the data in Fig. 4 show a lack of correlation between these fast relaxation components.

The short relaxing component is undoubtedly related to domains rich in paramagnetic impurities, and it is present in all samples. As previously shown, the presence of iron and other paramagnetic impurities is common to all our samples, as demonstrated by EPR spectra. These paramagnetic impurities are introduced in the manufacturing process. Consequently, the fast T_1 relaxing component related to paramagnetic impurities will be ignored in this context, and we will turn our attention to the slow T_1 relaxing component.

To characterize the nature of the



6. ^1H NMR spectra of a groundwood paper with neutral sizing at different temperatures. The sharp line on top of the broad one is from bound water, which is highly mobile even at low temperatures.

water and the energies associated with the motions of water binding and the cellulose internal motions, we performed a full T_1 (spin–lattice) relaxation study as a function of the

temperature. By this procedure, it is possible to quantify the amount of free and bound water (21, 22).

In all paper (7, 17) and cotton

samples, it is possible to measure the relaxation parameters of the cellulose simply by using the first few points of the magnetization measured in the time domain. Con-

Temp., K	LINTERS		KRAFT		GROUNDWOOD	
	Neutral	Acid	Neutral	Acid	Neutral	Acid
298	349±10	293±20	244±8	250±11	143±4	96±6
293	354±10	273±20	203±5	242±12	135±7	98±6
288	329±7	277±15	196±4	226±13	132±3	98±7
283	307±8	250±10	185±6	205±8	126±3	98±5
278	284±7	240±7	178±3	183±4	121±4	95±7
273	274±5	234±8	183±8	179±4	130±4	98±6
268	261±8	231±6	182±8	165±5	164±6	108±13
263	233±11	240±9	199±5	168±5	161±4	112±8
258	241±8	236±7	228±7	183±7	190±5	129±8
253	235±11	290±14	261±4	220±6	235±5	151±9
248	270±8	355±30	286±7	278±6	297±5	182±11
243	376±7	533±40	407±9	394±10	374±9	225±13
238	513±16	787±50	606±15	528±18	434±10	334±21
233	714±18	1026±100	815±25	774±24	466±11	360±30
228	1040±31	1581±100	987±45	978±27	559±17	445±35
223	1510±40	2102±160	1401±68	1277±63	613±16	489±35
218	2260±90	2742±180	1744±80	1688±70	659±25	520±42
213	3000±140	3243±200	2553±110	1823±73	710±33	603±50
208	3430±150	3475±300	3202±130	2393±100	728±34	651±52
203	4590±250	3273±240	4109±250	3010±250	799±38	672±52
198	6290±350	4078±370	4498±288	3371±250	808±40	672±50
193	7260±400	4991±300	5108±320	4040±300	850±40	617±60
188	8100±500	5341±400	5787±400	4390±350	906±48	692±50
183	9770±600	6451±450	7134±500	4590±400	906±50	645±45

III. T_1 spin-lattice relaxation times for the slow relaxing component of cellulose, milliseconds

versely, using points after at least 50 μ s, we derive only the relaxation parameters relative to the water component.

This observation is true until the temperature decreases to about 243 K, where the water resonance broadens and progressively merges into the broad cellulose resonance. As Fig. 5 indicates, the slow relaxing components of cellulose and water are strictly related by the spin diffusion process, which is still active at low temperatures.

Thus, even if the line width distinction (T_2) between the two components is present at a low temperature, as a result of spin diffusion, no T_1 distinction is observed. As Fig. 6 shows, the water peak can be observed down to about 218 K.

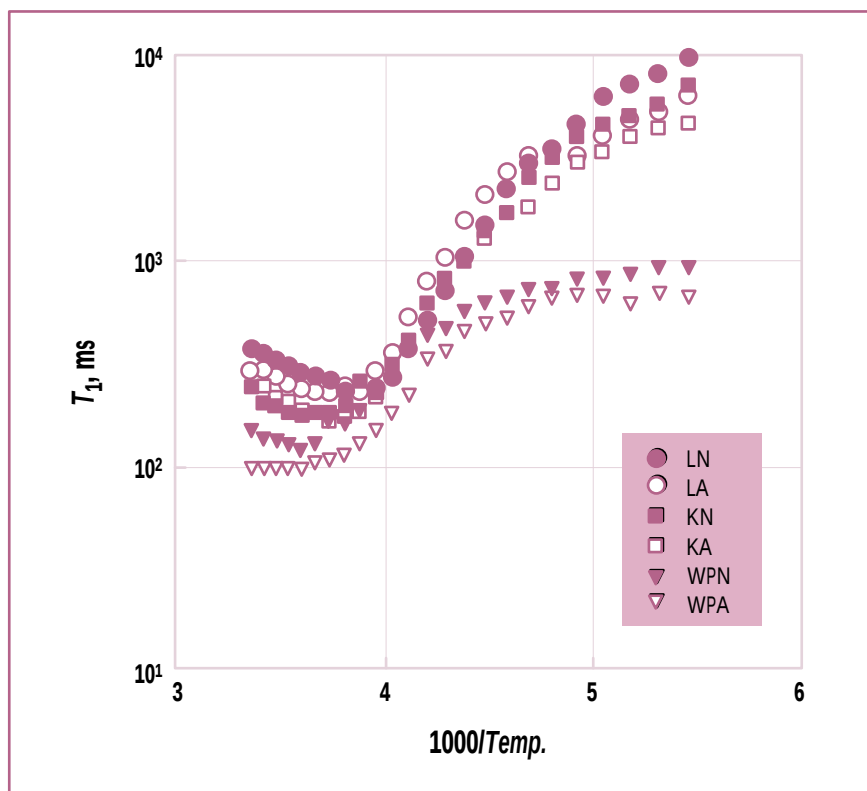
Furthermore, the freezing point of bound water is much lower than 273 K (23). In particular, we can

Sample	Relative amount of water
Linters	
Neutral	72
Acidic	69
Kraft pulp	
Neutral	88
Acidic	75
Groundwood pulp	
Neutral	100
Acidic	97
Ancient paper	68
Temperature of 298 K. Less than 2% error.	

IV. Relative amount of water as measured with a conventional spectrometer

Sample	Activation energy, KJ/mole
Linters	
Neutral	30.8±0.5
Acidic	29.0±0.8
Kraft pulp	
Neutral	26.9±0.9
Acidic	27.3±0.9
Groundwood pulp	
Neutral	22.0±1
Acidic	21.0±1

V. Activation energies for the cellulose-water system



7. Semilogarithmic plot of the long relaxing component of T_1 for cellulose vs. $1000/\text{Temp.}$ for all paper samples. T_1 relaxation times are quite distinctive, especially at low temperatures.

define different types of water in which the freezing point differs according to the type of hydrogen bonds and cellulose packing (5, 24). Different cellulose polymorphs and hemicelluloses are differently packed, and they contain different amounts of bound water, according to data reported previously (1, 3, 4, 7).

To clarify this point, we quantitatively analyzed bound water as a function of the temperature. We checked these results by using a different method to measure the relative amount of total water. This measurement was made with a high-resolution conventional spectrometer at 200.13 MHz. The data are listed in Table IV. The area has been set to 100 in the case of the neutral groundwood pulp sample, and all other integrals have been normalized with respect to this sample. The

relative amount of water measured at 57.0 MHz was found to be in good agreement with the relative amount of water measured at 200.13 MHz.

The most significant independent parameter that can be obtained from relaxometric measurements is the activation energy, as related to overall motions (segmental motions plus rotations) of the cellulose–water system. In fact, the bulk magnetic response and the motions of magnetic moments are correlated with the onset of molecular motions, which in turn are responsible for mechanical and dielectric losses (25). Thus, the measurement of T_1 as a function of the temperature can be used to give indications on the local stiffness and on correlation times associated with local motions (17). Data of this type are quite common in synthetic polymer physics, but these types of analysis

have not been attempted on paper samples. The results of a careful T_1 relaxation study on the cellulose signal as a function of the temperature are presented in Table III and Fig. 7.

In the low temperature range of 248–203 K, at the right side of the T_1 minimum where $w_0 t_0 \approx 1$, $\log T_1$ is linearly dependent on $1000/\text{Temp.}$ (Fig. 7). From this relationship, it is easy to obtain the activation energies for the overall motions of the cellulose–water system. The overall motion consists of segmental motions, rotations for the cellulose, and translations plus rotations for the water component. These values are listed in Table V.

One conclusion that emerges from the temperature dependence of T_1 relaxation for different samples is that all curves are distinct and separate. In particular, by comparing data for neutral or acidic sizing for each type of paper, we see that the acid sizing shortens T_1 relaxation times in the low temperature range, as Fig. 7 illustrates. At low temperatures, relaxation times are slightly shorter for all papers with sizing, with respect to their neutral counterparts. This slight decrease is probably caused by paramagnetic impurities contained in the acid sizing (rhombic Fe).

The energies presented in Table V are the Arrhenius activation energies for the overall motion of the cellulose–water system. In this system, many motions can contribute to the overall relaxation. If we think of cellulose as a polymer in which the overall chain motion is dominated by the rotations around the glycosidic bonds, we can reasonably assume that the higher the overall energy, the higher will be the order (crystalline content) and the orientation of macromolecules in cellulose fibers.

Besides the activation energy of cellulose, the other factor that contributes to the overall motion per-

KEYWORDS

Activation energy, bibliographies, bound water, cellulose, degradation, electron spin resonance, free water, nuclear magnetic resonance, paper, relaxation.

tains to the water, which is in spin diffusion with the cellulose. Again, a high activation energy of the water means a water with a tight bond to the cellulose. A lower energy means a loosely bound water molecule, such as a micro-drop of free water confined in a micro-hole.

Thus, the higher the overall activation energy, the higher the "quality" of the paper should be. This parameter is exactly the "cold" parameter needed to define both the physical quality of a paper sheet and its eventual degradation state after artificial aging or external contamination. Here the term "high quality"

is used in a strictly physical context. The term pertains to a paper sheet with cellulose as crystalline as possible and water as tightly bound as possible.

CONCLUSION

Paper can be thought of as a two-component material, made mostly of cellulose and water. This view is particularly useful in analytical studies carried out with proton NMR techniques. In this way, the nature and quantity of bound water can be substantially clarified. The effect of a particular sizing, for example, can be observed.

In the system of cellulose-bound water, the overall activation energies correlate well with the intrinsic merit of the paper ($E_{\text{linters}} \gg E_{\text{kraft}} \gg E_{\text{groundwood}}$). This measurement can be considered together with the total amount of bound water and the total amount of free water to define a quality factor. This quality factor

might be used in identifying criteria for the study of paper of different origins and for the study of artificial aging of paper. TJ

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