# The Interaction of Water with Cellulose from Nuclear Magnetic Resonance Relaxation Times

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ABSTRACT: Spin-lattice and spin-spin relaxation times of the cellulose-water system have been measured. Cellulose, bound water, and free water components have been separated from the free induction decays permitting $T_2$ of each of these components to be monitored as a function of moisture content. From the results a point of plasticization has been defined and is associated with the transition between primary bound and secondary bound water. This region is associated with swelling of the structure allowing increased mobility of the cellulose chains. Free water has been shown to exist even at low moisture contents with the amount of free water increasing dramatically above the point of plasticization. A physical model of moisture distribution has also been discussed.

It has been well established that part of the water sorbed by cellulose has properties which are markedly different from bulk water. Many different works have substantiated this conclusion[1-5] and a lot of effort has been directed at quantifying the bound water content for different types of cellulose samples. Most of the work has been carried out on cotton; however, there seems to be a lack of agreement on the exact amount of bound water present. Early calorimetric studies by Magne et al.[4] found transitions for nonfreezing water in Acala cotton at 4.3 and 18.7% moisture by weight. Ayer[6] in examining the adsorbed water of cotton fibers found a transition at 10% moisture. He suggested that all water below this content was primary adsorbed or bound water. Stamm,[3] from thermodynamic calculations on sorption isotherms for cotton, estimated the molecularly held water to be less than 5 or 6% of the moisture content which corresponds to a transition in the sorption isotherm at 40% relative humidity. Neal and Goring,[7] from thermal expansivity of cellulose, estimated the amount of destructured or bound water for cotton linters to be 0.04 g/g.

A number of nuclear magnetic resonance studies are also reported. Ogiwara[8] and Sasaki[9] have obtained results of 15-25 and 23% moisture, respectively, for the bound water content of cellulose. Child[10] measured the relaxation times of various types of cellulose. The molecular motions of sorbed water molecules were found to depend on the physical state and degree of crystallinity of the cellulose. A sorbtion mechanism was proposed in which chain attenuation occurred at a certain stage in the sorption process. Carles and Scallan[11] reported an upper limit for total bound water in cotton of 0.15 g/g. However, they point out that because of experimental difficulties the value quoted was only approximate. Stratton[12] measured the viscoelastic properties of cellulose as a function of relative humidity. From a maximum in the storage modulus the primary bound water content was reported as 3.5%. A review of the techniques applied and the bound water obtained by these techniques has been prepared by Boesen.[13] He reported an average value of bound water in cotton linters of approximately 0.12 g/g. This is the mean value of various test results.

The large influence of moisture on the physical properties or cellulose has formed the basis for our investigation into the cellulose-water relationship. The hypotheses which have formed the basis for this work are the following: (1) the amount of water contained in a cellulose system is a direct function of the microstructure of that system and consequently one should not expect to obtain identical results with different samples without normalization on the basis of accessibility of the structure; (2) the water contained within cellulose can be subdivided into different categories in which the properties of a specific type of water will be measurably different; and (3) the effects of the interaction of a specific type of water with cellulose will lead to dramatic changes in the physical properties of cellulose, specifically involving its mechanical, electrical, thermal, and optical properties.

## Experimental Section

**A. Preparation of Cotton Linters Samples.** The cotton linters used in this study were obtained from Buckeye Cellulose Corp. The samples contained 99.5% $\alpha$-cellulose, 0.5% $\beta$, $\gamma$, and pentosan. Inorganic impurities were less than 200 ppm. The viscosity average molecular weight was 338580 with a DP of 2090. The oven-dry density was 0.36 g/cm$^3$. The samples were soaked in distilled water for 2 days. The moisture contents were then reduced to the desired levels by exposing the wet samples to atmospheres of differing relative humidities which were generated in a desiccator over saturated salt solutions. After conditioning, the samples were placed in NMR tubes and allowed to equilibrate in the desiccator for another day or two. Prior to measuring the relaxation times the NMR tubes were sealed. On completion of the relaxation time measurements the exact moisture contents of the cotton linters samples were determined by oven drying under vacuum to a constant weight.

**B. Relaxation Time Measurements.** Proton spin relaxation times were measured by a Bruker SXP pulsed spectrometer. All spin-lattice and spin-spin relaxation times were measured at 90 MHz. The magnetic field was generated by a 12 in. Bruker shimmed electromagnet operated in the current regulated mode. The temperature was controlled to an accuracy of about ±1°.

Spin-lattice relaxation times were measured by the 180-$T$-90 degree pulse technique.[14] No significant deviations from exponential behavior were observed. Spin-spin relaxation times were obtained from the free induction decay following the 90° pulse. $T_2$ is given by $T_{1/2}/\ln 2$, where $T_{1/2}$ is the time required for the free induction decay to fall to one-half its initially observed value.

## Discussion and Conclusions

**Dry Cellulose.** The relaxation data of a dry cotton linters sample (Figures 1 and 2) show only one component. The $T_1$ minimum at 370 K and the transition at 280 K are probably related to the same molecular motions. The correlation frequencies $\nu_c$ for molecular motions are obtained from the following relations[16]

$$\nu_c \cong 2^{1/2}\nu_0 \quad \text{at } T_1 \text{ minimum} \tag{1}$$

$$\nu_c \cong \tfrac{1}{2}\pi T_{2\mathrm{LT}} \quad \text{at the } T_2 \text{ transition} \tag{2}$$

where $\nu_0$ is the resonance frequency and $T_{2\mathrm{LT}}$ is $T_2$ at the low-temperature side of the transition. If the transitions in $T_1$ and $T_2$ are due to the same molecular processes which are thermally activated and can be described by the Arrhenius relation then the activation energy for the molecular motion can be obtained from

$$\nu_c = \nu_0 \exp(\Delta E/RT) \tag{3}$$

where $\nu_c$'s are obtained from eq 1 and 2. Equation 3 gives an activation energy of 17.8 kcal/mol.

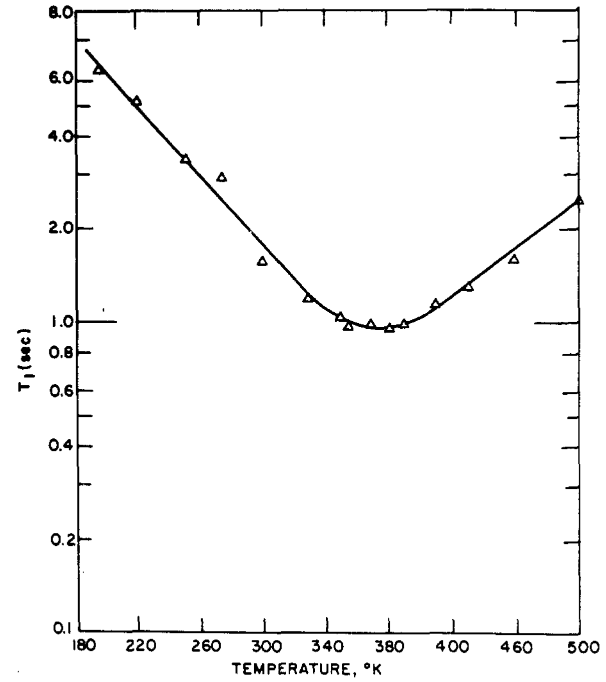

**Figure 1.** Spin-lattice relaxation time of dry cotton linters vs. temperature.

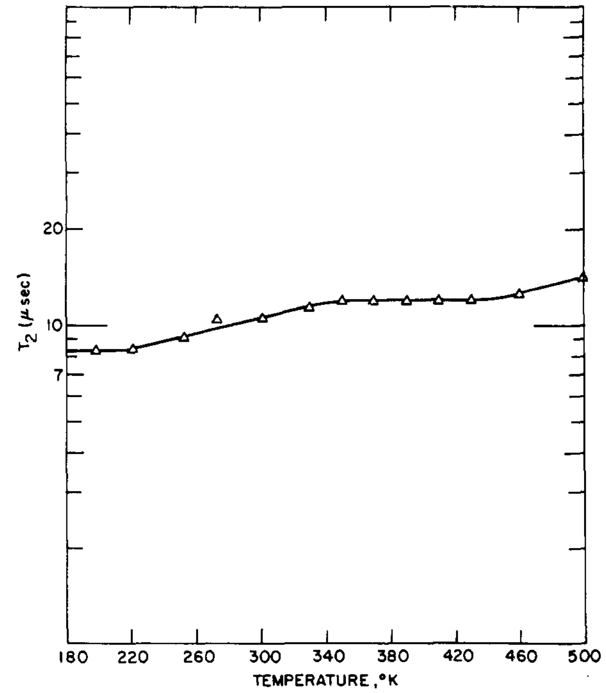

**Figure 2.** Spin-spin relaxation time of dry cotton linters vs. temperature.

In the crystalline regions of cellulose the chains are held together by cellulose–cellulose hydrogen bonds. This interchain bonding would result in rigidity of the crystalline regions which would not permit partial rotation of the anhydrocellulose rings without breaking hydrogen bonds. However, in the amorphous regions of the polymer, the decreased packing density of the chains probably permits the cellulose rings to undergo partial rotation. As such it is postulated that the $T_2$ transition at 280 K corresponds to the low-frequency components of the $T_1$ transition at 370 K and these transitions result from the partial hindered rotation of the cellulose rings in the amorphous regions of the polymer.

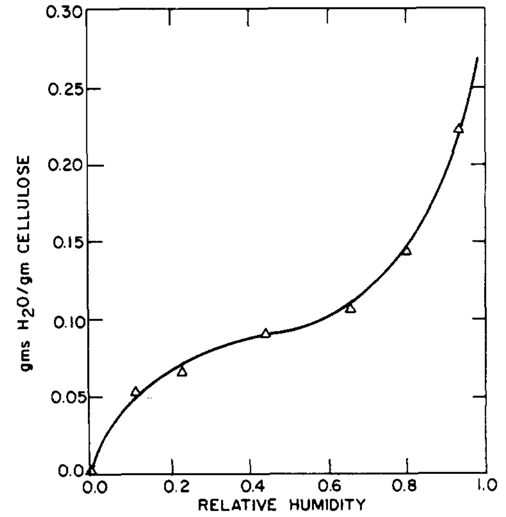

**Figure 3.** Sorption isotherm of cotton linters.

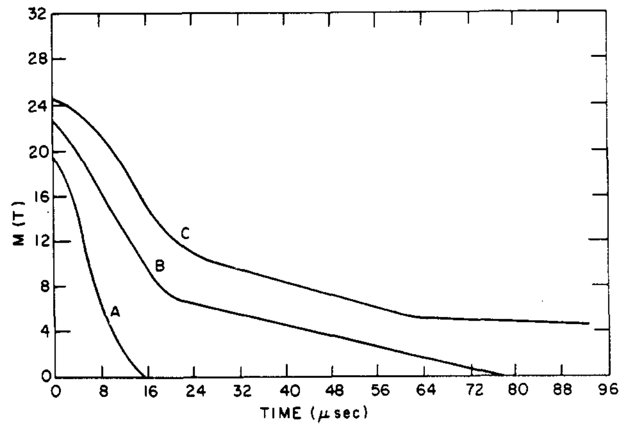

**Figure 4.** Free induction decay of cotton linters after 90°: (a) for dry cotton linters, (b) for cotton linters at low moisture contents, (c) for cotton linters at high moisture contents.

At 440 K $T_2$ again shows the onset of another molecular transition. The $T_1$ data do not extend to a sufficiently high temperature to show this transition. Measurement of the coefficient of thermal expansion of the 002 spacing of cotton cellulose shows a sharp increase at approximately 440 K.[17] This relaxation therefore may be due to some type of motion in the crystal lattice.

**Effect of Moisture on $T_1$ and $T_2$.** Figure 3 is a plot of water content versus relative humidity at room temperature for the cotton linters samples used. The plot is similar in shape to sorption curves for cotton linters obtained by other workers;[15] however, the water contents in the samples used in this study are higher than those previously found. This is probably due to the static nature of the conditioning environment. Nevertheless, in all attempts to relate moisture content to relaxation behavior the number of grams of water per gram of cellulose is used so that the actual amounts of water in the cellulose samples are utilized.

As pointed out earlier, the free induction decay (FID) for a dry sample of cotton linters contains only one component. Upon the initial addition of moisture, the FID is found to consist of two components while at higher moisture contents three components are observed; see Figure 4. The component with the shortest $T_2$ ($T_{2c}$) is assigned to the cellulose protons, the components with the intermediate $T_2$ ($T_{2b}$) to bound water, and the component with the

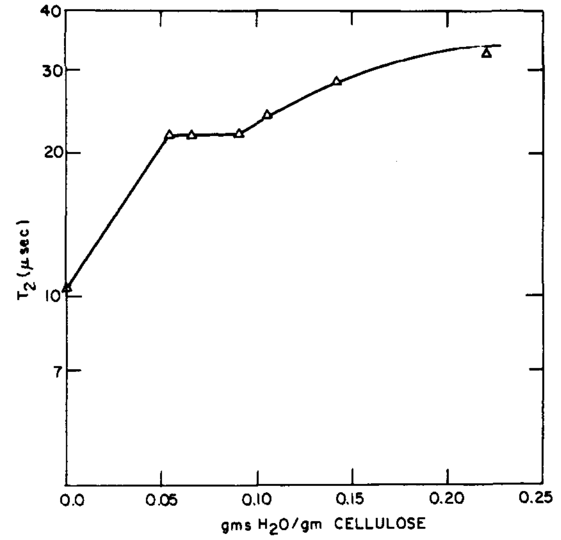

**Figure 5.** Spin–spin relaxation time of cotton linters protons ($T_{2c}$) vs. moisture content.

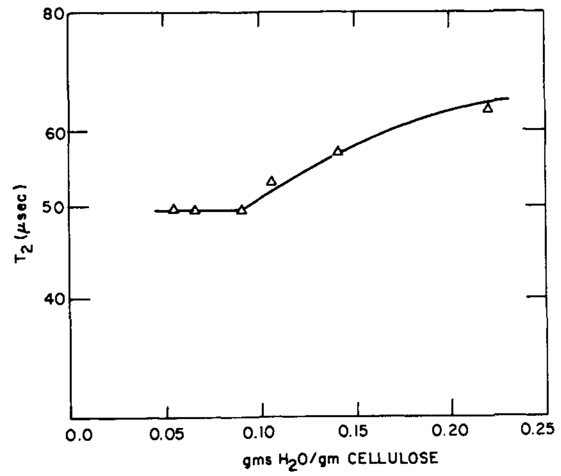

**Figure 6.** Spin–spin relaxation time of bound water ($T_{2b}$) vs. moisture content.

longest $T_2$ ($T_{2f}$) to free water. The actual $T_2$'s of the free water are not reported in this study. However, the amount of free water in each sample was estimated from the height of that component of the FID.

Figures 5, 6, and 7 show clearly that the addition of water to the dry cellulose system affects the molecular mobility of both cellulose and bound water. On initial addition of water $T_{2c}$ increases sharply with a corresponding sharp decrease in $T_1$. It should be pointed out that the slopes of the initial rise in $T_{2c}$ and the initial decrease in $T_1$ between 0 g/g and 0.05 g/g do not necessarily reflect the true slopes. No data were obtained for moisture contents lower than 0.05 g/g and as such the actual slopes may be steeper with the point at which $T_{2c}$ levels off occurring at a lower moisture content. Between 0.05 g/g and 0.09 g/g $T_{2c}$ and $T_{2b}$ are constant while $T_1$ decreases gradually. Above 0.09 g/g $T_{2c}$ and $T_{2b}$ increase and $T_1$ also increases sharply. $T_{2b}$ is greater than $T_{2c}$ due to the greater motional freedom of bound water over that of the cellulose chains. $T_{2b}$ is however of the order of 50 μsec indicating a vastly more restricted motion than free water which is approximately 700 μsec and bulk water which is approximately 3 sec. Many authors[15] have suggested that the initial adsorption of water by cellulose results from the bonding of water to unbonded cellulose hydroxyls and from the breaking of cellulose–cellulose hydrogen bonds with the formation of cellulose–water hydrogen bonds. If this is the case the cellulose chains will not be as rigid since the cellulose–cellulose hydrogen bonds which might act as pseudo-cross-linking sites and maintain rigidity of the chains are now broken and the chains are free to move. Moisture therefore disturbs the close proximity of the cellulose chains to each other, and as such reduces the intermolecular contribution to the dipole–dipole interaction. The acquired motion of the cellulose chains on water adsorption probably results in a small decrease in the intramolecular contributions. The combined effect of these two processes is an increase in $T_{2c}$.

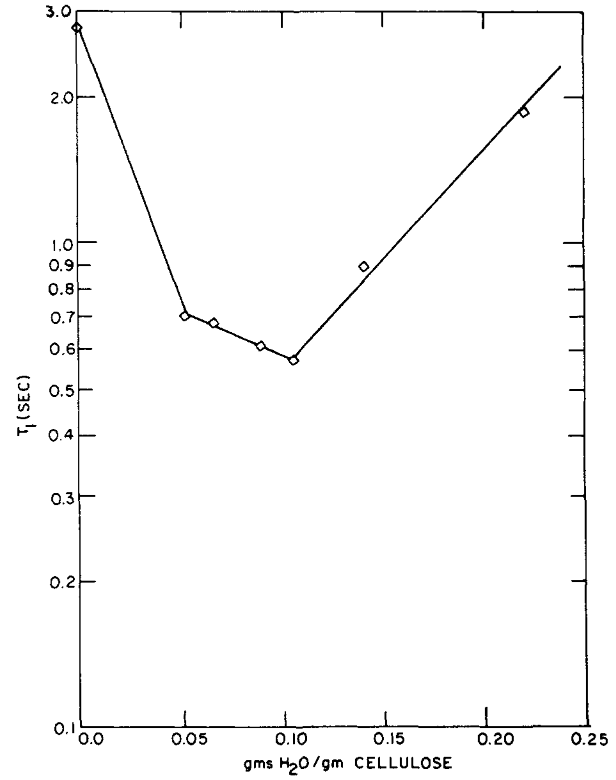

**Figure 7.** Spin–lattice relaxation time of cotton linters–water system vs. moisture content.

The water molecules which are tightly bound to cellulose will exhibit vastly restricted motion as compared to free water due to their close proximity to the cellulose chains. The tight bonding to cellulose along with restricted motion is responsible for the dipole broadened line of bound water and the resultant small $T_2$ as compared to bulk water. The leveling off of $T_{2c}$ and $T_{2b}$ above 0.05 g/g probably indicates one or a combination of several effects. This leveling may indicate that the molecular motions of cellulose and bound water at these moisture contents are too fast to affect the respective $T_2$'s or it may signal the attainment of maximum mobility for cellulose and bound water at these moisture contents and at this temperature. It is also possible that the adsorption of moisture between 0.05 and 0.09 g/g imparts no additional motion to cellulose or bound water since at these moisture contents the sorbed water is utilized in the satisfaction of unbonded cellulose hydroxyls and the breaking of interfibril hydrogen bonds.

Above 0.09 g/g moisture $T_{2c}$, $T_{2b}$, and $T_1$ all increase. We refer to this moisture content as the plasticization point above which both cellulose chains and bound water acquire added modes of motional freedom. It is suggested that on adsorption the system swells. After satisfaction of the more readily accessible hydroxyls further swelling will make available new hydroxyls from newly broken cellulose–cellulose hydroxyl bonds. The swelling and availability of hy-

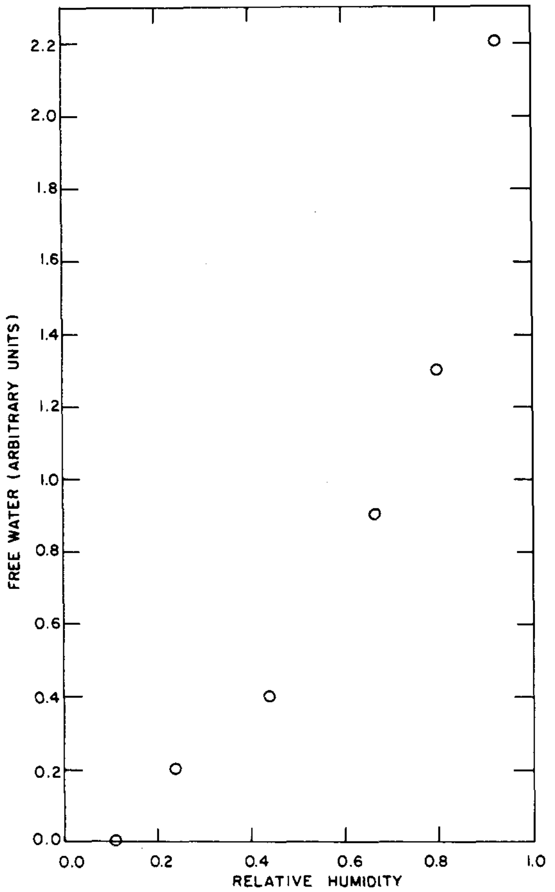

**Figure** 8. Free water content vs. relative humidity.

droxyls is limited however by the densely packed regions. Nevertheless the opening up of the structure allows the formation of multilayers of water. It is not surprising therefore that the point of plasticization coincides with the upturn in the adsorption plot of Figure 3.

The plot of free water versus relative humidity (Figure 8) provides evidence that even at very low moisture contents free water is present in small quantities. The fact that free water exists even below the point of plasticization, where one would normally expect it to begin to occur, suggests that there exist multilayers of water either at the surfaces or in microvoids in the fiber structure. Above the point of plasticization the amount of free water increases sharply lending support to the hypothesis of the formation of multilayers at higher moisture contents. Although the existence of free water at low relative humidities has been speculated on in the literature,[15] to our knowledge it has not previously been confirmed or shown to coexist with other "types" of water in cellulose.

The existence of free water in the system would result in swelling to such an extent that both cellulose and bound water would acquire additional modes of motion. This is observed above the point of plasticization. However, due to the restraints on the amorphous regions by the crystalline domains there will be a limit to the swelling. The molecular motions of cellulose and bound water will eventually attain maximum mobility such that one might expect $T_{2c}$ and $T_{2b}$ to again level off at some moisture content above the point of plasicization. Although our data do not extend to high enough moisture contents to unequivocally confirm this, it does appear that $T_{2c}$ and $T_{2b}$ are leveling off around 0.20 g/g moisture. This is in agreement with data reported by Swanson, Stejskal, and Tarleow[18] for a cotton sample where the second moment of the cellulose resonance was found to level off above 0.15 g of water/g of cotton. This transition point is defined as the total bound water saturation point and corresponds to the complete satisfaction of all cellulose hydroxyl groups which are accessible to water.

The existence of free water, whose correlation time for molecular motion would be much shorter than either bound water or cellulose, would enable the cellulose–water system to relax via the spin-diffusion mechanism.[10] $T_2$'s for the components are much shorter than $T_1$ hence nuclear spin energy can be transferred by diffusion from the more rigid cellulose protons to the more mobile molecules which in turn can effectively exchange this energy with the lattice. This would result in the rapid initial drop in $T_1$ followed by the more gradual drop up to 0.09 g/g. As the amount of free water increases, multilayers build up until those layers sufficiently far away from the cellulose surface acquire the motional freedom approaching that of bulk water whose rotational correlation time, $\tau_c$, approximates $10^{-12}$ sec. Thus $\tau_c$ is now too small to effectively relax the protons and $T_1$ increases. This is the case above 0.09 g/g moisture.

**Model.** Based upon the data obtained in this study the following model is proposed for the moisture sorption and distribution in cellulose. Cellulose in a dry state is a system of macromolecular chains held together by intermolecular hydrogen bonding in which the chains pass through both low ordered amorphous regions and highly ordered crystalline areas. Upon the initial addition of water, strong hydrogen bonding occurs between water molecules and active surface sites on the cellulose structure which may be unsatisfied hydroxyl groups. Since limited expansion occurs in the cellulose structure during this step $T_{2c}$ and $T_{2b}$ remain constant. It seems plausible that in the region where $T_{2c}$ and $T_{2b}$ level off sorption occurs on the intermolecular bonds between bundles of fiber rather than in the internal structure. This process continues until surface saturation is attained and in the case of our cotton linters sample occurs at 0.09 g/g which is defined as the point of plasticization and coincides with the upturn in the sorption isotherm. The initial moisture adsorbed in this way is called "Primary Bound Water".

Successive additions of moisture will now allow penetration of the fiber bundles or internal surface hydroxyl groups in the amorphous areas. As the water enters the structure, the system begins to swell markedly and creates void spaces for the formation of multilayers of water. This process continues until it is limited by boundaries established by the crystalline regions. This transition point is defined as the "Total Bound Water Fiber Saturation Point". The water which has hydrogen bonded to the internal surface hydroxyl group is referred to as the "Secondary Bound Water" while that water which has formed as multilayers is called the "Free Water". The incorporation of free water continues until the Fiber Saturation Point is reached at which time additional water begins to fill the large volume external to the cell wall (lumen) and this water is commonly referred to as "Bulk" water. In reference to previous literature on this topic, "Free Water" is the so-called freezing water while the primary and secondary sorbed water has been called nonfreezing water.

## Summary

Evaluation of the $T_1$ and $T_2$ relaxation times of a cotton linters–water system, obtained using a pulsed nuclear magnetic resonance technique, has produced the following results and conclusions.

1. A physical model of moisture distribution in cellulose

has been developed. The model is based upon the detection and identification of four types of water incorporated in cellulose: (1) primary bound; (2) secondary bound; (3) free; and (4) bulk.

2. A point of plasticization has been associated with the transition between primary bound and secondary bound water, and is associated with swelling of the structure allowing increased mobility of the cellulose chains.

3. Free water has been shown to exist at very low moisture contents with the amount of free water increasing dramatically above the point of plasticization. This says in effect that although the adsorption process involves different types of water at different relative humidities it is a combined process involving free water.

4. The primary implication of these results is that the incorporation of specific types of sorbed water will lead to dramatic changes in physical properties. From the results obtained one might expect large changes in the physical properties of the material above the point of plasticization. One would also expect the point of plasticization to depend on the material studied since the accessibility would vary.

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# N(1s) X-Ray Photoelectron and Electronic Absorption Spectra of Poly(squarylamides)

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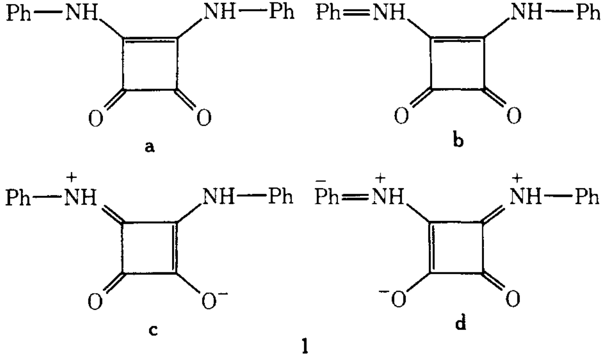
ABSTRACT: The products of polycondensation of *p*-phenylenediamine with either squaryl dichloride or squaric acid obtained in preceding work, containing either the 1,2-disubstituted or the isomeric 1,3-disubstituted cyclobutene ring system in the recurring unit, are investigated by X-ray photoelectron and electronic absorption spectroscopy. The findings are in agreement with highly delocalized electronic systems and indicate more than 50% iminium character in both polymer types. The cyclobutene-3,4-dione and cyclobutenediylium 2,4-diolate structures, respectively, employed previously for description of the four-membered ring moieties in the two polyamide isomers cannot, therefore, be regarded as valid structural representations, although the use of these and other structures with formally uncharged nitrogen atoms may be retained for convenience of drawing.

A recent study[2] of the two isomeric dianilides of squaric acid, 1 and 2, by electronic and X-ray photoelectron (ESCA) spectroscopy has revealed some rather striking structural features. In 1, the spectroscopic data point to canonicals **b–d** as major ground-state contributors, whereas the 1,2-dianilinocyclobutene-3,4-dione structure **1a**, commonly accepted to that day as a valid description, in fact represents but a minor contributing form. In 2, forms **c–e** are important, while **2a** and **2b**, both proposed as predominant canonicals in the earlier literature, carry minor weight in the hybrid. It is thus evident that both dianilides represent highly mesoionic systems possessing considerable iminium character.



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It is instructive to compare the charge distributions in these nonpolymeric amides with those in analogous polymeric squaryl amides of the types 3 and 4.[3] These polyamides, in keeping with common terminology in squaric acid chemistry,[4] were depicted in the quoted communications[3] by the dione and diolate structures **3a** and **4a**, respectively.[5] In view of the predominance of iminium structure in 1 and 2 it stands to reason, however, that the representations **3a** and **4a** do not reflect the actual distribution of charge in these polymers. In an effort to clarify the problem of charge distribution and assess the relative thermal stability behavior resulting from potentially different extents of