is also discussed, but no conclusion is possible at present. Further research in the structure and morphology of poly(aryloxyphosphazenes) is a subject of continuing investigation at this laboratory, with the goal of affording a more complete description of the molecular processes associated with the thermal transitions.

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The Effect of Temperature on the Cellulose/Water Interaction from NMR Relaxation Times

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ABSTRACT: An earlier investigation of the interaction between cellulose and sorbed water has revealed dramatic changes in molecular mobility at the point of plasticization. This transition region is associated with the satisfaction of primary adsorption sites and the resultant swelling of the system accompanying this condition. Many drastic changes in physical properties are predicted on the basis of this phenomenon. On lowering the temperature, the cellulose/water system continues to permit the determination of spin–spin relaxation times for a cellulose phase, bound water, and free water phases. The cellulose and bound water phases also exhibit plasticization which seems to require smaller amounts of moisture to attain this condition at lower temperatures. The freezing point of free water is lowered from 273 K for bulk water to between 221 and 252 K while freezing of bound water occurs at 196 K. Above room temperature the exchange prorcess, involving water molecules between the various phases, makes a large contribution to the T_2's observed. As a result a bound water phase can no longer be distinguished from the others. Increasing the temperature also probably opens the structure up making previously inaccessible sites available with the result that primary adsorbed water does not impart additional motion to the system above room temperature.

In a recent NMR study on the interaction of water with cellulose the molecular motion of the cellulose chains, bound water, and free water were monitored as a function of the amount of sorbed water in cotton linters.[1] In that study both the cellulose and bound water exhibited an increase in molecular motion at the point of plasticization. This plasticization point is associated with the transition between the primary bound and secondary bound water and results from the swelling of the structure allowing increased mobility of the cellulose chains.[1] Even though free water was found to exist at very low moisture contents the quantity increased dramatically above the point of plasticization where multilayer buildup is expected.[1] This is consistent with the upturn in the adsorption isotherm for the system.[1]

Following the dramatic effects which were observed at constant temperature, this study was undertaken to determine what added perturbations a temperature variable would impose on the cellulose/water system. As a result, the spin–lattice (T_1) and spin–spin (T_2) relaxation times of cellulose containing varying amounts of water were measured as a function of temperature.

Experimental Section

The cotton linters used and the method of treatment have been described previously.[1] The pulsed NMR apparatus and the techniques for measuring T_1 and T_2 are also described in an earlier publication.[1]

Results and Discussion

The relaxation times of cellulose/water systems were measured as a function of moisture content and temperature in the range 196 to 360 K. At temperatures below room temperature the T_2 behavior is similar to that reported previously where the free induction decays (FIDs) are observed to consist of a cellulose component (T_{2c}), a bound water component (T_{2b}), and free water (T_{2f}).[1] These features are found even at temperatures as low as 221 K, except that the free water phase disappears between 252 and 221 K. This is in agreement with previous observations where sorbed water was found to freeze within the same temperature range.[2] As pointed out earlier the freezing process is not indicative of ice formation but reflects only the reduction in molecular mobility which produces icelike behavior[2] in the free water component. At temperatures below the freezing of free water T_{2c} and T_{2b} are still observed. Figure 1 contains plots of T_{2c} and T_{2b} as a function of moisture content at 221 K. The plots are typical of T_{2c} and T_{2b} for temperatures below room temperature. T_{2b} is still larger than T_{2c} reflecting the greater motional freedom available to bound water as compared to the cellulose chains.

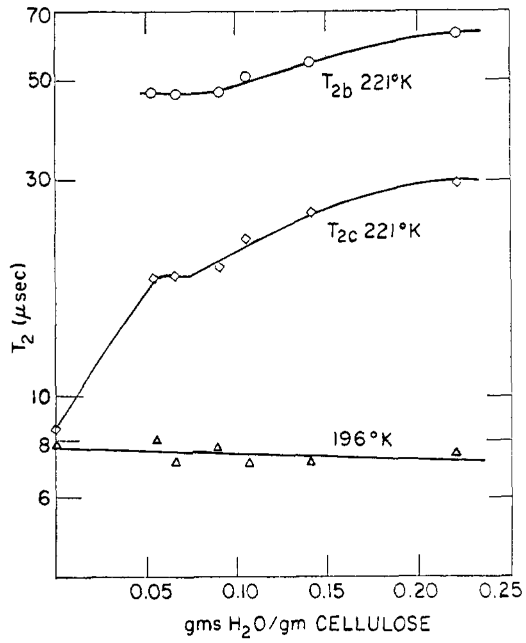

Figure 1. Spin-spin relaxation times of cellulose (T_{2c}) and bound water (T_{2b}) at 221 K and T_{2c} at 196 K vs. moisture content.

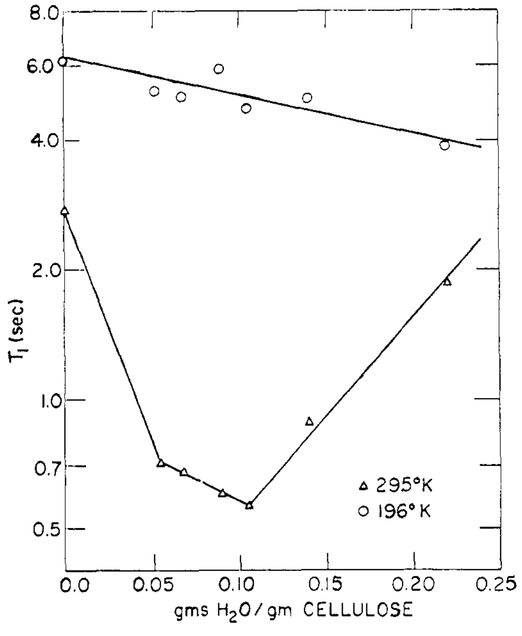

Figure 2. Spin-lattice relaxation times (T_1) of the composite cellulose/water system vs. moisture content at 295 and 196 K.

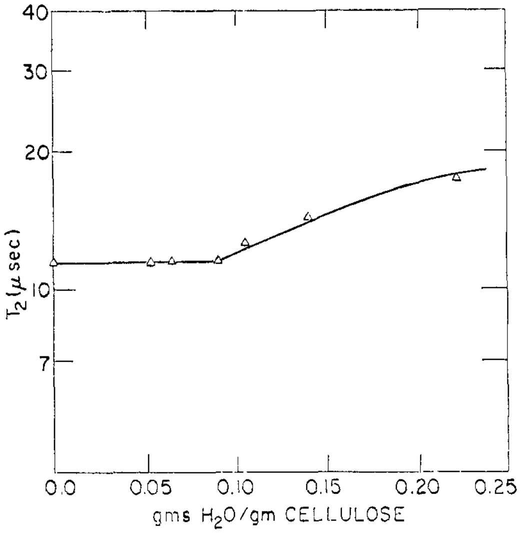

Figure 3. Spin-spin relaxation time of cellulose (T_{2c}) vs. moisture content at 310 K.

The point of plasticization is observed between 0.08 g/g and 0.09 g/g in T_{2c} and T_{2b} and it appears to shift to slightly lower moisture content with decreasing temperature. However, there are not enough data points between 0.06 and 0.09 g/g to unequivocally draw such a conclusion.

At 196 K the FID is exponential, consisting of only one component. At this temperature, neither free water nor bound water components are observed (see Figure 1). The T_1 plots of the composite cellulose/water system at 295 and 196 K are given in Figure 2. The minimum observed in the 295 K plot is not found at 196 K. As a matter of fact, the T_1's at 196 K are about an order of magnitude larger and show only a slight decrease with increasing moisture content. This is consistent with the apparent insensitivity of T_2 to the sorbed water content. As pointed out earlier, the motions of free water are frozen out above 221 K. Free water is somewhat removed from the cellulose surface and although the freezing point is lower than that of bulk water, it is higher than bound water. This reflects the much more intimate interaction of bound water than free water with cellulose. As a result, it is expected that bound water will freeze at a lower temperature. At 196 K the T_{2c} and T_{2b} components cannot be distinguished. This may be due to the fact that T_{2c} is approximately equal to T_{2b} or it may result from a total loss of amplitude of the bound water component on loosing its motional freedom at freezing. At 221 K, T_{2b} is at least twice the magnitude of T_{2c}. If on lowering the temperature the bound water phase becomes more rigid, its motions would be less free, resulting in longer correlation times for those molecular motions thereby giving rise to much shorter T_2's. It is anticipated therefore that the T_{2c} and T_{2b} can approximate each other as the motions of the bound water are frozen. As a matter of fact, at 196 K the motion of the cellulose component itself is drastically reduced. The frequency of the partial hindered rotation of the anhydroglucose units in the amorphous regions is much less than 10^4 Hz at this temperature, and cellulose exhibits its rigid lattice value for T_2.[1] At this low temperature there is also a lack of efficient relaxing sites which were provided by the more mobile free water and bound water components at higher temperatures. The effect of the spin-diffusion mechanism is minimized with the result that the T_1's are long and a minimum is not observed. Therefore it can be concluded that at 196 K there is a drastic decrease in the mobility of the molecular network with a resultant decrease in the ability of water to swell the fiber at this low temperature.

As the temperature is increased above room temperature, the bound water phase cannot be distinguished from free water. The resulting FID consists of two components, a cellulose and free water phase. Figure 3 gives a plot of log T_{2c} vs. moisture content at 310 K. The overall T_{2c}'s are about one-half the values at room temperature and this trend continues at higher temperatures. Another interesting feature is that the initial steep rise in the T_{2c} plot between 0 and 0.05 g/g for temperatures between room temperature and 196 K is absent. T_{2c} is fairly constant between 0 and 0.10 g/g. It should be pointed out that as the temperature is increased above 300 K, there is evidence, through fog formation on the walls of the NMR tabe, of the removal of moisture from the samples. T_2 values of free water as a function of temperature show a region of slightly increasing T_2's for cotton linters above 283 K.[2] Samples of Whatman CF1 paper gave T_{2f} values which decreased slightly above 288 K.[2] These results were interpreted in terms of exchange of water molecules between high energy or tight binding sites and secondary sorbtion sites with less binding energy.[2] Our results can be interpreted in a similar manner. At temperatures below 295 K, T_{2b} and T_{2f} are sufficiently different ($T_{2c} \sim$ 8–30 μs, $T_{2f} \sim$ 700 μs at 295 K)[2] and the rates of exchange between the phases are slow enough to permit the observation of the two phases separately. As the temperature is increased, the rates of exchange between the phases increase rapidly and the distinction between the phases can no longer be made. The T_2 mechanisms now include a contribution from the exchange process which increases with temperature, giving rise to an eventual minimum in T_2 or a plateau region depending on the distribution of barrier heights to exchange.[3] It therefore appears that as the temperature is increased exchange of water molecules between the bound water phase and free water becomes rapid thereby making the distinction between the two impossible. The decrease in T_{2c} at the higher temperatures cannot be explained at this time except to postulate that as the temperature is increased the cellulose structure opens up probably allowing exchange between the tightly bound phase and the newly created sites. The fact that the initial steep rise in T_{2c} observed at lower temperatures is not found for samples above room temperature also tends to suggest that as the structure opens up and the intrinsic processes of the cellulose chains become fairly rapid the primary adsorption process (up to the point of plasticization) does not impart additional motion to the system.

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Configurational Thermodynamic Properties of Polymer Liquids and Glasses. Poly(vinyl acetate). II

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ABSTRACT: The theoretical internal energy, entropy, and internal pressure of the equilibrium system of poly(vinyl acetate) using the scaling parameters established previously are computed as functions of temperature and pressure and found to be in good agreement with those derived from the experimental PVT data given in paper I. For the analysis of the glassy state, a new method is developed and applied to the two constant formation glasses discussed earlier. It employs the partition function which has the same mathematical form as for the equilibrium system, but derives the hole fraction $h(V, T)$ as the solution of a partial differential equation. This equation results from the proper thermodynamic definition of the pressure in terms of the partition function, applied to the experimental PVT surfaces for the glasses. A quantitative improvement in the compressional thermodynamic functions, particularly in regard to the internal pressure, ensues over the more empirical procedure employed previously. There h is treated as an adjustable parameter in the pressure equation derived for the liquid, using the experimental PVT surface for the glass. The application of the proper expression for the pressure results in a reduced variation of h with temperature and pressure in the glassy state and thus in numerically larger freezing fractions than those derived earlier. We exhibit the internal energy and entropy differences between the atmospheric pressure and pressurized (800 bar) glasses, and between these and the super-cooled melt. The computed difference between the configurational heat capacities of the melt and glass at T_g are about 47% for C_p and 13% for C_v of the totals obtained by calorimetry. Finally, convenient interpolation expressions for the hole fraction, theoretical internal energy, and theoretical entropy as functions of the reduced variables of state are developed for the equilibrium liquid in general and the two specific glasses considered here. These relations dispense with the necessity of iteration procedures for the numerical evaluation of the theoretical functions.

In a recent paper[2] (paper I) we have analyzed the liquid and glassy states of polymers in terms of theory and based on experimental data for poly(vinyl acetate).[3] The discussion was concerned with the PVT (pressure–volume–temperature) relations applicable to the liquid (equilibrium) region and glasses formed by variable and constant formation histories. With the variable formation history the properties of the glass are obtained by isobaric cooling at one constant rate at different pressures always commencing at temperatures sufficiently large to attain initial equilibrium. The intersection of the extrapolated liquid and glass PVT surfaces gives the proper glass transition temperature $T_g(P)$. With the constant formation history the glass is formed by isobaric cooling at one pressure P' (0 or 800 bar) with subsequent measurements in the glass being made at additional pressures. The intersection of the liquid and glass surfaces gives $T_g^{\dagger}(P,P')$. Since all data points of the constant formation glass pertain to one formation pressure P', and since no structural relaxation was observed after glass formation, the corresponding PVT surface is taken to be reversible, yielding proper thermodynamic quantities even though true equilibrium is not attained. For further details, see ref 3. The discussion in paper I encompasses first the liquid equilibrium state, second the liquid–glass transition line and the relationship between the pressure coefficients $\mathrm{d}T_g/\mathrm{d}P$ and $\mathrm{d}T_g^{\dagger}/\mathrm{d}P$ of glasses formed under the variable and constant formation histories, respectively, and third the equation of state for the glasses of the latter kind. Of central importance in this analysis is the behavior of the ordering parameter y, the fraction of occupied sites, in the three regions mentioned above.

The purpose of this paper is to present a discussion of the configurational thermodynamic functions, in particular those which can be derived from PVT measurements and compared with theoretical predictions. We have previously shown some