The Determination of Moisture Transitions in Cellulosic Materials Using Differential Scanning Calorimetry

ROBERT A. NELSON, *Xerox Corporation, Webster, New York 14580*

Synopsis

The association of water with cellulose is of significant technological importance. It forms the basis for the manufacturability of paper and ultimately controls, either directly or indirectly, mechanical, electrical, thermal, and optical properties. Differential scanning calorimetry has been used to characterize moisture transitions in these materials. Total bound water contents have been determined. Specific transitions for the model system, cotton linters, have been identified including free water incorporation point (0.05 g/g), total bound water (0.18 g/g), and fiber saturation point (0.05 g/g). Results are compared to those found in a pulsed nuclear magnetic resonance study in which a moisture distribution model was generated; free water point (0.046 g/g) and total bound water (0.19 g/g). The differential scanning calorimetry technique can provide a more readily available, less expensive, and simpler technique for paper/cellulose characterization and study.

INTRODUCTION

The interaction of water with cellulose is of prime technological importance. It forms the basis for the manufacturability of paper and ultimately controls, either directly or indirectly, mechanical, electrical, thermal, and optical properties. Although considerable effort has been expended[1,2] toward an understanding of this relationship, no single acceptable theory of moisture sorption of cellulose has yet emerged.

In a previous paper,[3] it was shown that the specific moisture distribution in cellulose at any moisture content could be detected and identified via pulsed nuclear magnetic resonance spectroscopy (NMR). A model of moisture sorption and distribution for four types of water was presented. These were defined as (1) primary bound, (2) secondary bound, (3) free, and (4) bulk water.

Three distinct moisture transitions were also shown to exist. The first occurred with the beginning incorporation of free water. The second occurred upon the filling of primary bound sorption sites and corresponded to the moisture plasticization point of the material. The third occurred upon the satisfaction of secondary bound water. The moisture content at this third transition is equivalent to the total bound water content of the system. It is this transition point which will be addressed primarily in this paper.

Extensive literature is available on total bound water determination, and readers are referred to a previous paper[3] and references contained in it for a more complete review. Suffice it to say that earlier attempts in areas of solute exclusion,[4,5] nonsolvent water,[6–13] nonfreezing water,[14–16] rate of cooling,[17] rate

of drying,[18,19] heat of wetting,[20–23] and desorption isotherm[24,25] analysis were all shown to determine the bound water of cellulosic materials.

More recent work has been fostered to some extent by the idea that water can be considered an equilibrium mixture of strongly hydrogen-bonded clusters and monomeric molecules.[26] This concept was furthered by Ramiah and Goring[27] who proposed that a cellulose surface could act as a structure breaker of water, and consequently would be covered by a monolayer of water. The primary implication of this concept was that the bound water would exhibit properties which were markedly and measurably different from the remaining water present in the system. This proposed difference provided the impetus for additional studies of the concept of bound water using sophisticated techniques capable of detecting and measuring these differences.

Recently,[28] high-resolution nuclear magnetic resonance (NMR) spectroscopy has been used to examine the line width of water resonances as a function of moisture content in cellulose structures. From the line widths obtained, attempts have been made to calculate the amount of bound water present. It has even been shown,[3] using the technique of pulsed NMR, that in addition to detecting bound water, it has been possible to identify three types of water associated with cellulose, two of which can be considered "bound."

Specific physical property changes, including dimensional stability, conductivity, and thermal effects, have also been related to the incorporation and interaction of particular types and amounts of water within cellulose. A major drawback to the use of NMR and, in particular, pulsed NMR is the large initial cost of equipment which affects its availability and the necessity of having a knowledgeable operator. It was primarily for this reason that differential scanning calorimetry was investigated for its ability to determine moisture distribution transition points in cellulosic samples.

This study indicates that the DSC technique has the capability of detecting and quantifying moisture transitions in cellulosic materials. The correlation of these transitions to specific physical property changes could lead to an invaluable technique for cellulose and paper characterization both as a research and quality control tool.

EXPERIMENTAL

Samples

Studies were performed on seven cellulosic samples: (1) cotton linters (obtained from Buckeye Cellulose Corporation) of 99.5% alpha cellulose, 0.5% beta, gamma, and pentosan, less than 200 ppm inorganic impurities, viscosity-average molecular weight 338,580 with a D.P. of 2090, oven-dry density 0.36 g/cc; (2) Southern hardwood kraft pulp; (3) Southern softwood kraft pulp; (4) unsized paper (the Hammermill Paper Company); (5) sized paper (the Hammermill Paper Company); (6) starch sizing (the Hammermill Paper Company); (7) Whatman #1 filter paper. All samples were soaked in distilled water for two days to bring them to the desorption curve of the sorption isotherm. The samples were then brought to successively lower moisture contents by exposure to low relative humidity. Exact moisture contents were determined at the end of each experiment by oven drying (105°C) under vacuum to constant weight.
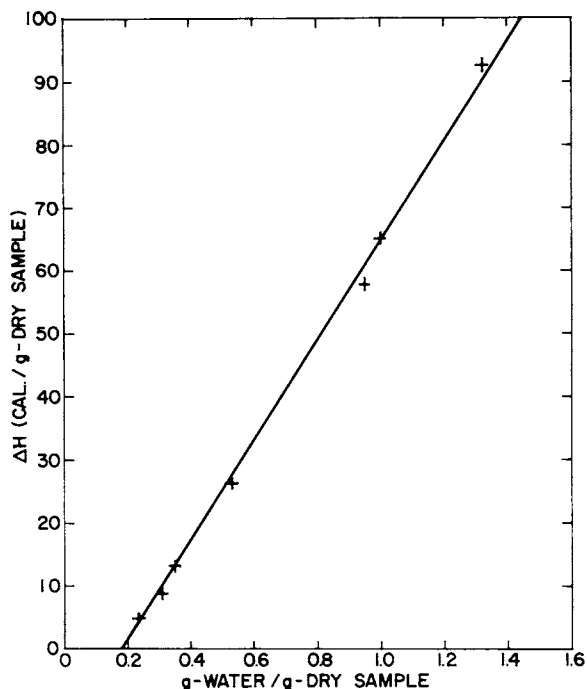
Fig. 1. Enthalpic heats of melting vs. total water content for cotton linters.

Differential Scanning Calorimetry (DSC)

The differential scanning calorimeter was a Perkin–Elmer DSC-1B. The unit was temperature programmed at a rate of 10°C/min and the results recorded on a chart recorder. A sample of distilled water was used to calibrate the temperature scale (correction factor, −9°C). Temperature plots are corrected to true freezing point of water. The area under the endotherm curve (enthalpic heat of reaction) at a specific chart speed and DSC sensitivity range was used to establish a correction factor (assuming for water, $\Delta H_F = 79.7$ cal/g) which was cross checked with an indium standard to assure accuracy. Samples were contained in sealed aluminum sample pans and quickly cooled with liquid nitrogen to −80°C in the DSC. Results were recorded as the temperature was increased just through the ice-melting endotherm.

RESULTS AND DISCUSSION

The concept of freezing and nonfreezing water to evaluate the interaction of water with cellulose was first applied in 1947 using basic calorimetry techniques.[14] That water which was contained in the cellulose structure and would not freeze was considered as "bound" with energies greater than those involved in the water-to-water hydrogen bond. The remaining water, which would undergo freezing, was suggested to behave similar to bulk water. On this assumption, Magne et al.[14] found that two thermal transitions could be detected using calorimetry techniques. The first transition defined a water content below which none of the water would freeze. The adsorbed water below this transition was
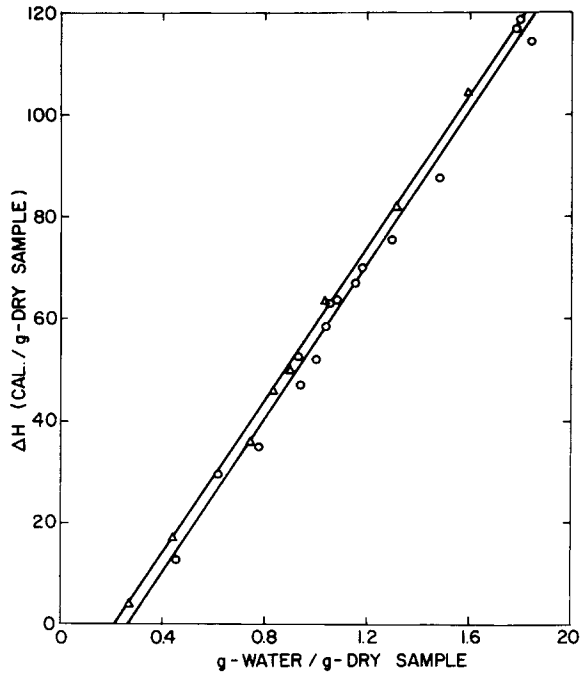
Fig. 2. Enthalpic heat of melting vs. total water content for (△) hardware and (○) softwood pulp.

called "bound water." A second transition was observed at higher water contents above which all additional water would freeze. The intermediate moisture range contained both freezing and nonfreezing components. The nonfreezing water of this intermediate range was not considered bound but rather water which was formed in multilayers or in small pores.

It is this second transition which was examined with DSC and which is presently considered the transition for "total bound water." Techniques[29] used previously have one major drawback in that they are typically time consuming, both in experimental and mathematical manipulation. The DSC technique, on the other hand, simply involves the calculation of the enthalpic heat of melting (ΔH_F) of the freezable water using the area under the endothermic curve. These values, obtained at various water contents, are then plotted against the total water in that sample. If the data are accurate, the points should fall on a straight line with a slope equal to the heat of fusion of bulk water ($\Delta H_F = 79.7$ cal/g). Extrapolation to $\Delta H = 0$ intercepts the water content axis at a point which is the *total bound water* content of that sample.

Figures 1–4 show experimental data for the seven samples. The data plots are indeed linear with slopes approximately equal to 79.7 cal/g. The total bound water content as determined by extrapolating to $\Delta H = 0$ is given in Table I. Using the value for cotton linters (0.18 g/g), relative comparisons can be made to results available in the literature. These include (1) 0.15 g/g,[28] (2) 0.23 g/g,[11] (3) 0.20 g/g,[14] (4) 0.175 g/g,[17] and (5) 0.20 g/g.[22] Considering the structural variations possible in those cotton linter samples studied as well as the relative accuracies of the various techniques employed, the total bound water determined
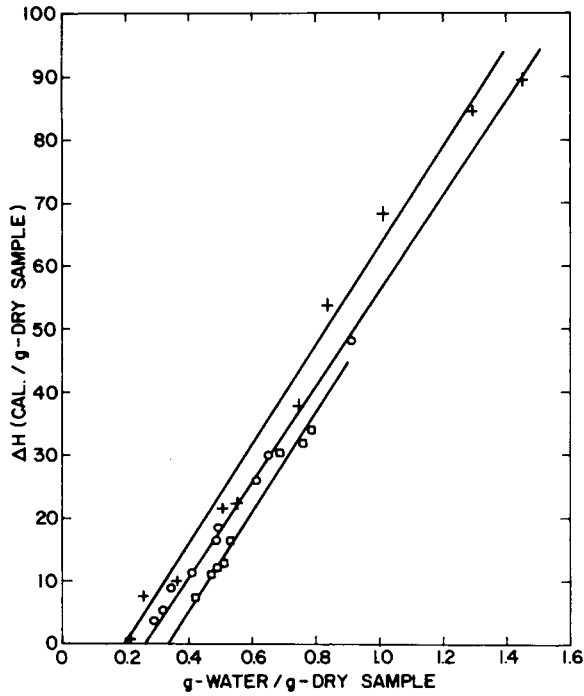
Fig. 3, Enthalpic heat of melting vs. total water content for (+) unsized paper, (O) sized paper, (□) starch sizing.
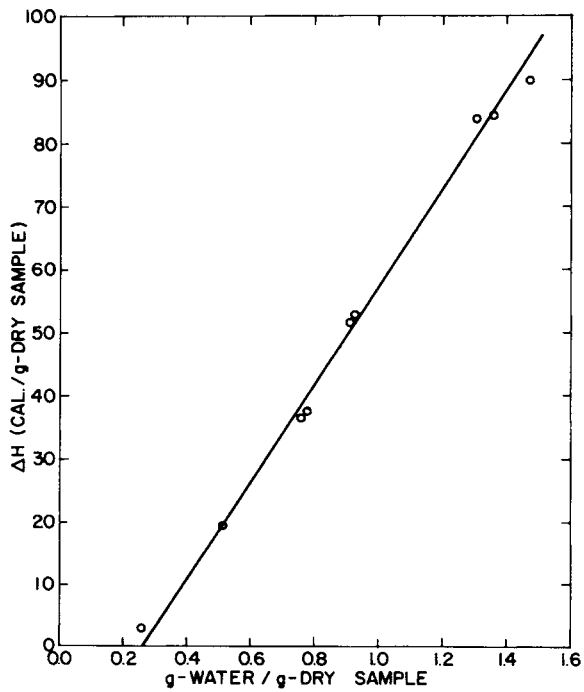

Fig. 4. Enthalpic heat of melting vs. total water content for Whatman #1 filter paper.

here would seem to be quite reasonable. As further evidence for the accuracy of the DSC technique, the reader is referred to a previous paper[3] in which pulsed NMR was used to study the cellulose/water interaction using the same cotton linters sample. The data for T_2 of bound water also show a transition at 0.190 g/g. Considering the differences in techniques, there is good agreement in the results.

Considering the total bound water values in Table I, it is important to note the distinctions made possible among samples using this technique. The unsized and sized paper and starch sizing provide a good example. The unsized base paper exhibits a total bound water content of 0.21 g/g, while the sized paper (manufactured with the same pulp and additives on the same machine) has a total bound water content of 0.23 g/g. The variation between these results (small but repeatable) must be associated with the sizing material used in the finished paper. In fact, the sizing does exhibit the much higher bound water content of 0.33 g/g. This material, which is primarily processed starch, has a much more amorphous structure than cellulose and consequently has an increased accessibility to water. Similar arguments based upon structural differences and corresponding water accessibility can be applied to all samples.

In fact, the DSC technique can be used to determine the accessibility of any material if an assumption is made concerning the water molecules associated with a particular reactive site. In the case of cellulose, which contains anhydroglucose as the fundamental unit, assumptions[28] have been previously made that one water molecule is associated with each accessible hydroxyl group. Using the reverse argument of Carles and Scallan,[28] where the fraction of accessible hydroxy groups of cotton was taken as 0.40 and the water-to-hydroxyl ratio was assumed to be 1, the total bound water content can be used to calculate the sample accessibility. If this is done for cotton linters, one obtains

$$0.180 \times \frac{162}{18} \times \frac{1}{3} = 0.54$$

as the fraction of hydroxyl groups accessible to water by hydrogen bonding (where 18 and 162 are the molecular weights of water and anhydroglucose, respectively). The accessibility should not be taken as an exact measure of the amorphous content of the sample, for hydroxyl groups at the interface of the crystalline areas would also be available.

Evaluation of the melting endotherm curve maxima, total water, and free water content for the various samples has shown that it is also possible to identify two additional transitions. As an example, the data in Figure 5 show a plot of the

TABLE I
Total Bound Water Content of Various Cellulosic Materials

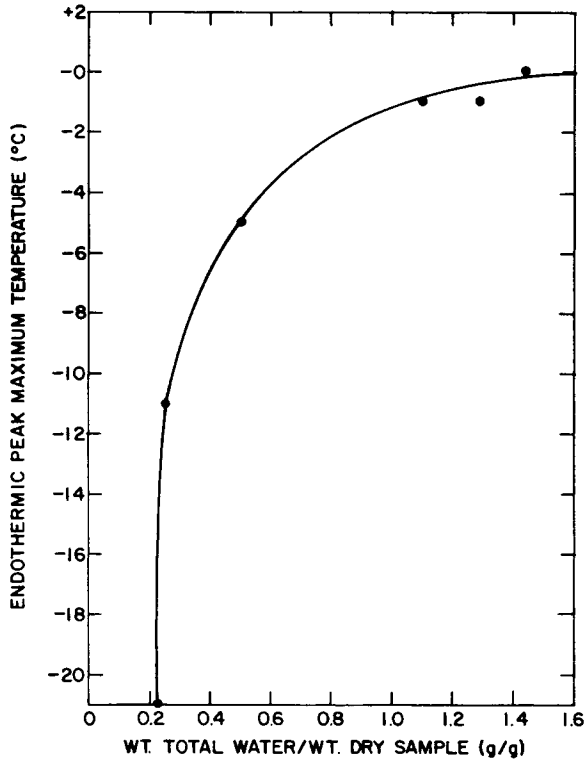| Sample	Total bound water, g H_2O/g dry sample
Hardwood pulp (kraft)	0.210
Softwood pulp (kraft)	0.255
Whatman #1 filter paper	0.265
Unsized paper	0.210
Sized paper	0.230
Starch sizing	0.330
Cotton linters	0.180

Fig. 5. Freezing temperature vs. total water content for unsized paper
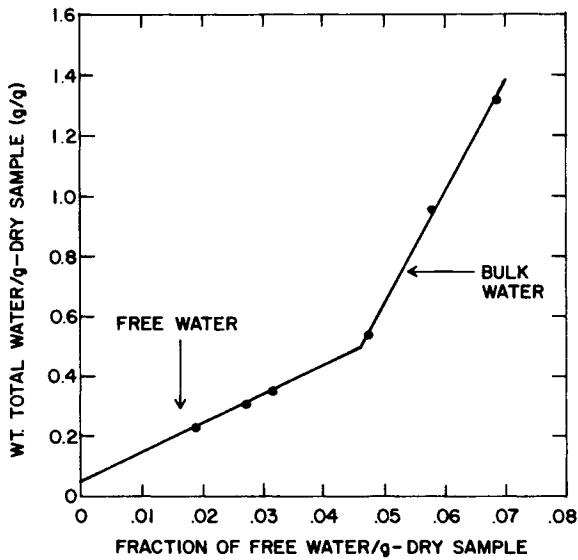

Fig. 6. Total water content vs. fractions of free water for cotton linters.

freezing temperature versus the weight of total water per gram of dry sample for the unsized paper. As the total water content decreases, a relatively sharp drop is evident in the freezing temperature. This is analogous to the theory of freezing point depression, even though it does not follow the conditions of dilute solution.
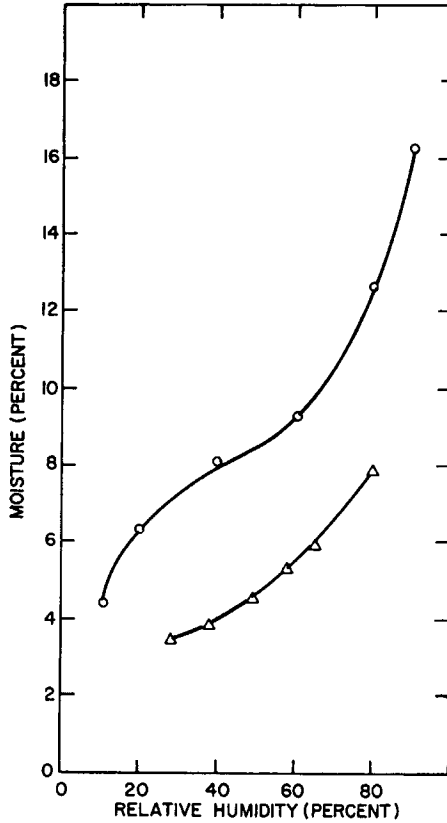
Fig. 7. Sorption isotherms. Cotton linters, 23°C.

At the higher total water contents, the freezing point (corrected) is equivalent to that of normal (bulk) water. The transition to lower freezing temperatures is due to water being destructured by interaction with the cellulose. In other words, this water is probably that contained within the cell wall. This has been defined previously as "free" water as opposed to "bulk" water which exists outside the cell wall. The transition, therefore, defines the "fiber saturation point" of the sample. Since the transitional areas as examplified in this figure are rather broad and knowing that free water is the contributing factor in the freezing exotherm, the data for cotton linters have been replotted (Fig. 6) as the weight of total water per gram of dry sample versus the fraction of total water present that exists as free water per gram of dry sample. The observed fiber saturation point transition is now much more distinct, giving a value of approximately 0.50 g total water per 1 g dry sample. This compares quite favorably with a published[28] fiber saturation point of a cotton linters sample (0.50 g/g) using the solute exclusion technique.[30]

The data in Figure 6 also indicate a second transition. Extrapolation of the free water portion of the curve to zero free water fraction intersects the total water content axis at a value of 0.05 g total water per 1 g dry sample. This is apparently the free water incorporation point and, based upon previous studies,[3] occurs
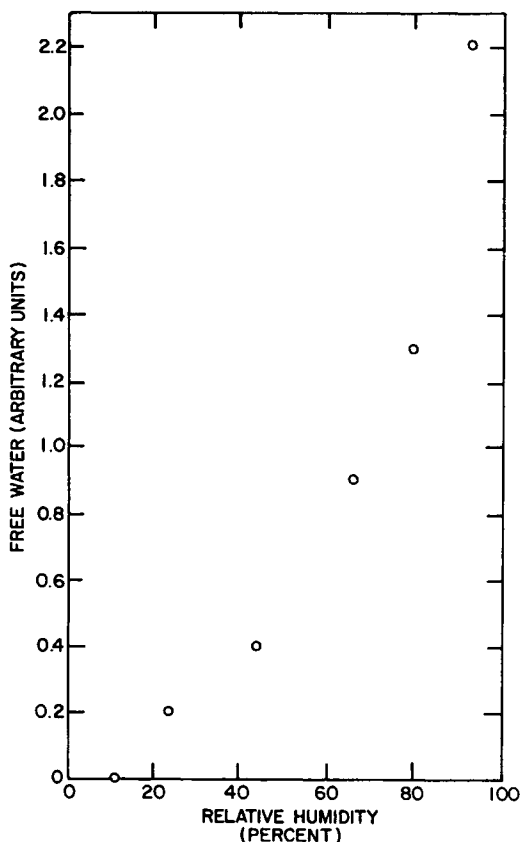
Fig. 8. Free water content vs. relative humidity.

before the moisture plasticization of cellulose (0.09 g/g) which is the saturation of primary bound water sorption sites. This free water incorporation point can be compared to that obtained using pulsed nuclear magnetic spectroscopy[3] on these same samples. The value of 0.05 g/g is equivalent to 4.7% total water. Using the sorption isotherms as shown in Figure 7, a 4.7% moisture content is obtained at approximately 12% relative humidity on the desorption isotherm. This value can then be compared to the free water incorporation point as determined by NMR (Fig. 8) which was about 11% relative humidity. Considering the difference in techniques, the agreement is very satisfactory.

CONCLUSIONS

The use of DSC for determining the total bound water of cellulosic samples has been shown to be a highly accurate and simple technique. Carried to an extreme, it might be argued to be a one-datum-point method when using well-equilibrated samples under ideal conditions.

When using a series of samples representing a large moisture content range, it is also possible to quantify the free water incorporation point, total bound water transition, and fiber saturation point. Confirmation of the ability of DSC to

quantify all the important moisture transitions for all cellulosic samples is required before general use is promoted. The ultimate use will depend on the development of specific moisture transitions/physical property relationships which will be reported on in a future paper.

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