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Hydration and swelling of pulp fibers measured with differential scanning calorimetry

Thad C. Maloney and *Hannu Paulapuro*, Helsinki University of Technology, Laboratory of Paper Technology, Finland, *Per Stenius*, Helsinki University of Technology, Laboratory of Forest Products Chemistry, Finland

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SUMMARY: This study describes a new differential scanning calorimetry (DSC) method, based on the isothermal melting of water, which may be used to measure hydration and swelling phenomena in pulp fibers. Nonfreezing and melting temperature depressed water (freezing bound water) are considered. Nonfreezing water is probably related to the number and type of accessible hydration sites. Both solution and pore effects may cause the melting temperature of water in the cell wall to be depressed.

Experiments with xylans with differing charge and drying history indicate that the isothermal melting technique can be used to measure the swelling of the gel phase in heterogeneous hydrated systems, such as pulp fibers. In previously-dried cotton it is found that the sum of nonfreezing and freezing bound water is equal to the fiber saturation point measured with solute exclusion. For never-dried unbleached kraft pulp a significant part of the water within the cell wall melts at the same temperature as bulk water. A likely interpretation is that such water is located within macropores, formed when lignin is dissolved in pulping.

ADDRESS OF THE AUTHORS: Helsinki University of Technology, P.O. Box 6300, FIN-02015 HUT, Finland

When water is absorbed by pulp fibers both the properties of the water and the cell wall are modified. The cell wall swells and becomes plastic which has important implications in the manufacture of paper for both water removal efficiency (Swerin et al. 1990) and product quality (Laine 1996). The amount of swelling and the physical properties of the swollen cell wall are influenced directly by the hydration of the fiber's polymer components. The term 'hydration' is often used and misused in the paper industry to describe various aspects of swelling and fiber/water interaction. It can be used as a technical term to describe the dewatering properties of a pulp or more appropriately in the context of direct water binding to the fiber surface. In this paper hydration will be used in a more general sense to describe the process by which the cell wall absorbs water and alters its thermodynamic properties.

It is the purpose of this study to introduce a new differential scanning calorimetry (DSC) technique which can be used to measure the amount of hydration water in pulp fibers and to apply the method to an unbleached kraft (ubk) pulp and some common wood polymers. Determining the amount of hydration water with DSC is based on the measurement of the energy absorbed when the water in a frozen sample of pulp fibers is melted. For saturated pulp fibers and other hydrated polymer networks the melting enthalpy of water in the sample appears to be smaller than for an equivalent amount of bulk water. One way to interpret this result is that some of the water in the sample does not freeze. A common feature of hydrated macromolecular networks is that in addition to nonfreezing water they contain some water that has a depressed melting temperature as well as water which melts at the normal temperature of bulk water.

In heterogeneous hydrated systems, where the melting temperature of some of the water in the sample is depressed far below that of bulk water, separate depressed and bulk water peaks are formed which can readily be evaluated with DSC (Hornshaw 1981; Ishikiriyama et al. 1995a). For saturated pulp fibers the amount of depression is so small that the depressed and bulk water peaks can not be easily resolved (see Fig. 1). Water absorbed in pulp fibers which melts at a depressed temperature shall be referred to as freezing bound water (FBW). In the DSC technique used in this study the water in the pulp fibers is melted isothermally at incremental temperatures approaching 0°C. This allows for the freezing bound water, the pore size distribution and the activity of the absorbed water to be calculated for pulp fibers.

The mass fraction of nonfreezing water (NFW) can be calculated with eq. [1] in which W_w and W_s are the masses of the water and dry solids, ΔH_t is the energy absorbed when the ice in a frozen pulp sample is completely melted (the dynamic endothermic peak area, Fig. 1) and ΔH_m is the specific heat of melting for bulk water. All water fractions are expressed in grams of water per gram of oven-dried solids.

$$NFW = (W_w - \frac{\Delta H_t}{\Delta H_m}) \frac{1}{W_s} \qquad [1]$$

It is assumed in eq. [1] that the melting enthalpy of water in the fiber wall is the same as that of bulk water and that no process other than the freezing of water contributes to the measured enthalpy.

There have been several theories proposed to explain why sorbed water does not freeze, though most of these are intuitive in nature. It has sometimes been suggested that the first 1 to 3 layers of water adjacent to a surface do not freeze because the molecules are already in a configuration resembling ice or are otherwise bound in the respect that their motions are severely limited (Berlin et al. 1970). It is well known that the molecules in the first layer of water on a surface may be oriented by electrostatic or hydrogen bonding interactions. However, it has been shown in a number of studies (Galin, Galin 1992a,b; Stapf 1996) that the motions of the water molecules in at least the outer layer of nonfreezing water are quite similar to the motions in bulk water.

It has also been suggested (Deodhar, Luner 1980) that in pulp fibers there is a minimum pore size (4 nm, corresponding to -4°C) below which water can not freeze. However, in this study melting is detected in pulp at much lower temperatures. Plouchly et al. (Plouchly et al. 1979) believe that the inability of water to freeze in hydrated gels is strictly due to kinetic effects. According to Plouchly, at the temperature below which no more water freezes (about -12°C for wood pulp) or at the moisture ratio (MR) when no water freezes (about 0.25 g/g) the diffusion of water is so slow that ice can no longer form.

One way to consider nonfreezing water is with the site adsorption theory. This approach has recently been taken by Berthold (Berthold 1996) in an attempt to explain swelling of hemicellulose gels. Berthold assumes that nonfreezing water is adsorbed onto both acid and hydroxyl groups. Since the largest proportion of hydrophilic sites in pulp fibers are hydroxyl groups, most of the nonfreezing water is adsorbed here. Other studies (Nakamura et al. 1981; Hatakeyama et al. 1987; Kabeya 1993) also indicate

that the amount of nonfreezing water is directly related to the number of accessible hydroxyl groups, measured as crystallinity. For a pulp which has undergone purely physical processing, changes in nonfreezing water may indicate changes to the pulp's cystallinity, while in cases where the fiber chemistry has been altered changes to other possible adsorption sites must also be considered. The site adsorption theory is rather simplistic as it does not take into account such factors as the orientation of the hydroxyl groups which are known to affect hydration (Franks 1978).

The thermodynamic theories which might explain the temperature depression of water in the fiber wall fall into one of two categories: those that treat the cell wall as a porous solid and those which consider the cell wall components to be partially solubilized. The melting temperature depression of water in porous solids is a well-studied phenomenon (Rennie, Clifford 1977; Homshaw 1981; Jackson, McKenna 1990; Ishikiriyama et al. 1995a,b; Ishikiriyama, Todoki 1995a,b; Ishikiriyama et al. 1996). If it is assumed that the pores in the fiber wall contain pure water, the melting point of the water will be depressed due to the increased pressure within a small body bounded by a curved interface with surface tension σ_{ls}. The relationship between the radii of curvature of the surface and the melting point depression is described by the well-known Gibbs-Thompson equation. NMR studies (Li 1993) indicate that the pores in the fiber wall are elongated along the fiber axis with a length of several microns. Hence it seems reasonable to assume that they are elongated capillaries. Neglecting end effects, the boundary between ice and water is assumed to be cylindrical with radius r. The Gibbs-Thompson equation thus takes the form:

$$r = \frac{-V_m \sigma_{ls}}{\Delta H_m \ln \frac{T}{T_0}} \qquad [2]$$

Where V_m is the specific molar volume of ice and T_0 is the melting point of water at normal pressure. The calculated pore size will depend on the selection of σ_{ls}, for which numerous wide-ranging values can be found in the literature (Hobbs 1974; Rennie, Clifford 1977; Ishikiriyama et al. 1995a). The value for σ_{ls} which Ishikiriyama (Ishikiriyama et al. 1995a) derives for the melting of ice in porous silica media at 0°C in cylindrical pores, 20.4 mN/m, is used in this study.

The swollen cell wall can also be viewed as a mixture of partially soluble polymer and water. In that case the melting point depression is caused by a lowered activity and increased entropy of the water in the water/polymer mixture. If pore effects are neglected, then for a well-washed pulp it may be assumed that salts and other low molecular weight substances have a negligible effect and that the high molecular weight amorphous components contribute to the melting point depression of water within the cell wall. The activity of water, a, as a function of melting temperature for a hydrated gel is given by (Plouchly et al. 1979):

$$\ln a = \frac{\Delta H_m}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \frac{\Delta C_p}{R}\left(\frac{T_0}{T} - 1 + \ln\frac{T}{T_0}\right) + \frac{b}{2R}\left(T - \frac{T_0^2}{T} + 2T_0 \ln\frac{T_0}{T}\right) \qquad [3]$$

Where R is the gas constant and ΔC_p is the change in heat capacity when water freezes. For the constant b the value 7.95×10^{-3} J/(K^2.mol) is used.

Materials and methods

DSC measurements

DSC measurements were carried out on a Mettler DSC 30. The principle of the isothermal melting technique is to raise the temperature in a frozen sample to a preset value where it is held constant until the melting transition is completed. The sample is then immediately cooled down and the melting is repeated at a slightly higher temperature. In this study the following thermal sequence was used: cooling to -45°C, heating at 5°C/min to -30°C and holding for 5 minutes and then re-cooling to -45°C. The cycle was repeated with the isothermal melting set point at -8, -5, -3, -2, -1, -0.6, -0.4, -0.2, -0.1 and 0°C for the calibration sample with enough time for melting to complete. The final temperature scan was a dynamic measurement from -30 - +15°C used to determine ΔH_t. A considerable hysteresis was noted if the freezing/melting cycle was repeated several times, the reason for which remains unclear. Hysteresis was minimized with the above thermal sequence because the sample is entirely frozen and melted only twice. In a dynamic DSC measurement thermal delays in the sample make it difficult to determine the temperature range over which a transition really occurs (see Fig. 1). In isothermal melting, because the temperature is held constant until the melting transition has completed, thermal delays are avoided.

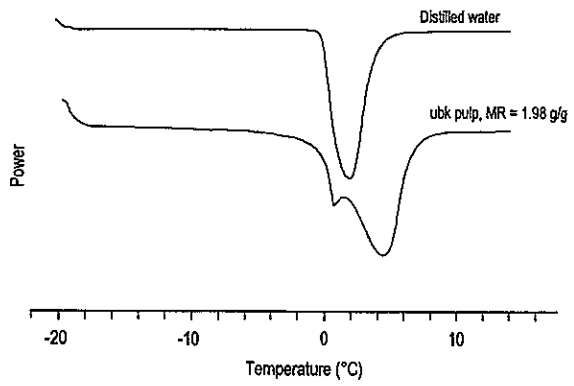

Fig. 1. The dynamic endotherms for both pulp fibers and distilled water. Water within the fiber wall with a depressed melting point is visible as a sub-peak, but the resolution is insufficient for direct evaluation. Note that thermal delays cause the bulk water peak for the pulp sample to be shifted to a higher temperature than for the distilled water sample.

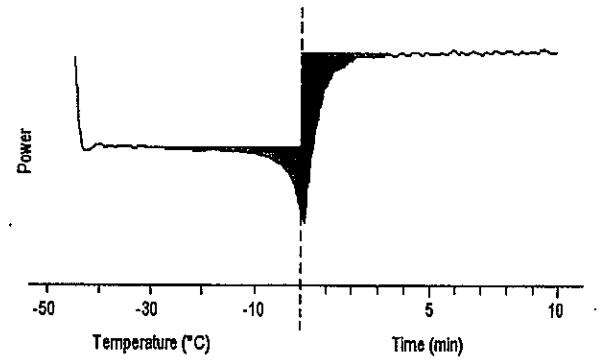

Fig. 2. Endotherm for a sample of unbleached kraft pulp at MR = 1.18 g/g with isothermal melting at -0.2°C. The shaded portion minus a blank reading at -30°C is the total energy involved in the melting transition, ΔH.

The energy involved in melting, ΔH, was determined by integrating the endotherm shown in Fig. 2 and subtracting a blank value determined by taking a measurement at -30°C, well below the lowest temperature at which melting is observed. It was found that when isothermal melting is carried out at 0.5°C for either distilled water or saturated pulp fibers the measured enthalpy constantly matches the enthalpy from a dynamic measurement (-30 - +15°C) within 5%. This suggests that the accuracy of the isothermal melting measurement is in this range. The precision of the isothermal melting measurement depends on the sample and the melting temperature. Precision decreases as the melting temperature approaches 0°C and is worse for samples which display a high degree of melting in a narrow temperature range. For most pulp samples the precision of the melting temperature depressed water ranges from about ±0.01 g/g at lower temperatures to about ±0.1 g/g at -0.1°C. In this study all measurements were done in duplicate and the average is reported.

Calibration was performed by applying the above sequence to 5 samples of distilled water ranging in weight from 0.2-2.5 mg. ΔH_m was calculated from linear regression of the mass-ΔH_t curve as 405.3 ± 1.8 J/g. This value was used in eqs. [1] and [4] instead of adjusting the internal calibration of the DSC. This method allows calculation of NFW for pulp with a precision better than ± 0.02 g/g. The literature value for ΔH_m of 333 J/g was used in eqs. [2] and [3]. Temperature calibration was carried out by plotting the average fraction of energy absorbed in isothermal melting, $k = \Delta H/H_t$, as a function of temperature as shown in Fig. 3. The point at which the sample completely melted was taken as 0°C.

It has been known for a long time that ice will absorb energy near 0°C, prior to melting completely (Hobbs 1974). The effect of melting in the bulk phase may be accounted for if it is assumed that bulk water in a saturated pulp sample behaves the same as the calibration sample. This allows for the weight fraction of melting temperature depressed and nonfreezing water, W, at each isothermal temperature to be calculated according to eq. [4].

$$W = \frac{\Delta H - (\Delta H_t - \Delta H)k}{\Delta H_m \cdot W_s} + NFW \qquad [4]$$

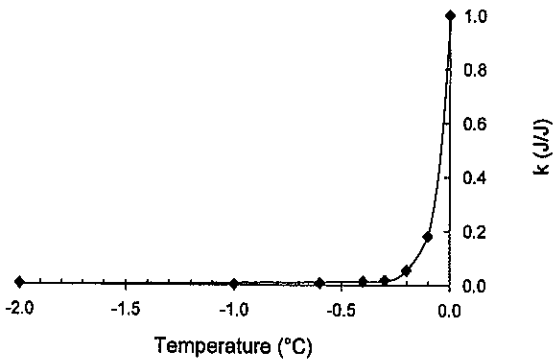

Fig. 3. The relative energy absorption, k, as a function of temperature for distilled water. Average of 5 samples.

The fiber saturation point (FSP) has been shown to be a good estimate of the amount of water held within the cell wall (Stone, Scallan 1967). The FSP was determined by solute exclusion as the amount of water inaccessible to a 2,000,000 Dalton dextran polymer.

Materials

1 g of commercial never-dried unbleached kraft pulp was washed thoroughly with distilled water to remove dissolved substances. The acid groups in the cell wall were exchanged to the sodium form by heating a 1% slurry of the pulp in 0.1M sodium acetate for 1 hour at 40°C. The pulp was then rewashed several times with distilled water and centrifuged at 3000g for 10 minutes to adjust the moisture ratio close to the fiber saturation point.

The sample of lignin was purified from pine kraft black liquor. It has an average molecular weight of 5200 Daltons. Two xylans of differing charge content were used. The highly charged xylan sample (xylan-hc) was isolated from kraft pine bleached with an oxygen-peroxide sequence. Its total acid group content is 9.0% (moles acid per mole of xylose). The xylan-lc sample was isolated from kraft pine bleached with an oxygen-chlorine dioxide sequence. Its total acid content is 0.5%. The details of the isolation and structures of the xylans are found elsewhere (Mitikka-Eklund 1996). Two types of cellulose were used: thoroughly washed commercial grade cotton and Whatman grade cc31 microcrystalline cellulose.

After centrifuging, 2-2.5 mg of the wet ubk pulp was sealed in a 40 µl preweighed aluminum sample pan. The other samples, except those in Fig. 7, were prepared by adding 1.2 mg of distilled water to 1 mg of the air-dried sample with a microsyringe. The samples were then sealed, weighed and allowed to equilibrate overnight at room temperature. The samples in Fig. 7 were adjusted to MR = 2.3 g/g and the "twice dried" xylan-lc sample in the same figure had an additional drying/rewetting sequence. The mass of dry solids was determined after drying overnight at 105°C.

Results

The pore size distribution calculated from the Gibbs-Thompson equation for the ubk sample is shown in Fig. 4. For the "corrected" curve the values of k found in Fig 3 are used in eq. [4] and for the "uncorrected" curve k = 0. Subtracting the melting of bulk water from that of the saturated fibers closes the pore size distribution on the right. The total bound water (TBW) is defined as the water which either does not freeze or melts at -0.2°C. This is the onset of the level portion of the of the distribution and is indicated by "TBW" in Fig. 4. For all remaining pore size and activity distributions the mass fraction of water, W, is calculated with eq. [3] using the values of k found in Fig. 3.

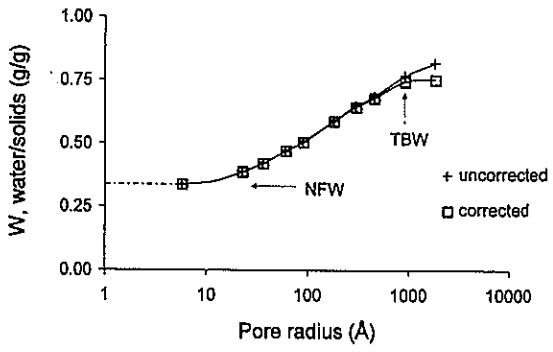

Fig. 4. The pore size distribution for ubk pulp. The corrected curve shows the effect of subtracting the melting of bulk water in the pulp sample. Nonfreezing water (NFW) and total bound water (TBW) are marked in the figure. MR = 1.18 g/g.

Table 1. Summary of DSC pore size distribution and solute exclusion data for ubk, cotton and microcrystalline cellulose samples.

sample	MR	NFW	FBW	TBW	FSP	Bulk Water in cell wall	Aver. pore radius
	g/g	g/g	g/g	g/g	g/g	g/g	nm
ubk	1.18	0.34	0.41	0.74	1.35	0.44	22
cotton	1.19	0.24	0.12	0.36	0.36	0.00	10
microc	1.05	0.20	0.14	0.34	---	---	16

The FSP for the ubk pulp was 1.35 g/g (see Table 1). At the moisture ratio which the DSC measurement was done, 1.18 g/g, all the water in the sample should be contained within the cell wall. Since the total bound water is 0.74 g/g, it can be concluded that a significant amount of the water contained within the cell wall has thermodynamic properties similar to that of bulk water. A likely interpretation of this result is that the bulk water is contained within gaps outside the amorphous gel. It is generally accepted that the cell wall of wood pulp fibers consists of cellulose microfibrils packed in a ligno-hemicellulose gel (Scallan 1974; Kerr, Goring 1975). These in turn are organized into sheets of "interrupted lamellae" (Kerr, Goring 1975). When lignin and hemicelluloses are dissolved in pulping gaps are formed between the lamellae which allow the cell wall to expand and contract as the swelling conditions change. The water between the lamellae is outside the amorphous regions, in pores with a radius of curvature approaching that of the pulp fiber. Under these conditions melting temperature depression is not expected.

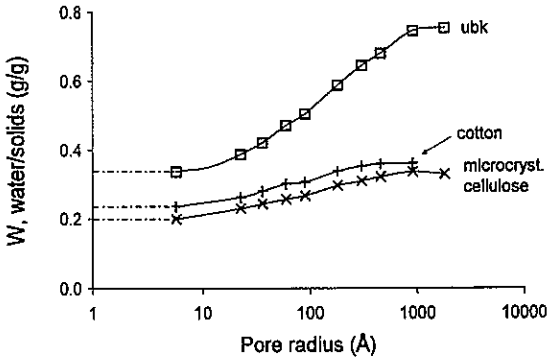

Fig. 5. The pore size distribution for ubk, cotton and microcrystalline cellulose.

Supporting evidence for this hypothesis is found by comparing the total bound water and the fiber saturation point for a sample of once-dried cotton. The drying should have caused the larger interlamellar pores to collapse, so that any water contained in the cell wall is held within small pores either between the cellulose microfibrils or within their amorphous regions. It is expected that all the water within the wall of the cotton fiber will melt at a depressed temperature. The results from this experiment are summarized in Table 1 and excellent agreement between total bound water and fiber saturation point was obtained. The pore size distribution for the cotton, the micro-crystalline cellulose and the ubk pulp are shown in Fig. 5. The weighted average pore size, neglecting the thickness of the nonfreezing water layer, was calculated and is shown in Table 1. As expected, the ubk sample has a somewhat larger average pore size then either the microcrystalline cellulose or the cotton. The average pore size for the ubk sample from the DSC method is considerably larger than has been reported from solute exclusion measurements (Stone, Scallan 1967), but in this respect one must keep in mind the fundamental differences between the two methods.

In order to illustrate the effect of hemicelluloses on the melting temperature of water the ubk sample is compared to two samples of xylan with differing charge. For these samples the amount of water per gram of solids is expressed as a function of 1-a where a is calculated from the melting temperature according to eq. [3]. This is shown in Fig. 6.

The curves in Fig 6 are similar to sorption isotherms which have been used for years to characterize pulps and other materials. However, there are some important differences. One difference is that the measurements are done at different melting temperatures, so the curve is non-isothermal. Another distinction is that the isothermal melting technique allows for the spectrum of activities to be measured at any moisture content at which water freezes. For sorption isotherms the moisture content of the sample is determined at a given vapor activity, which does allow for the activity of the already-adsorbed water to be determined as a function of moisture content.

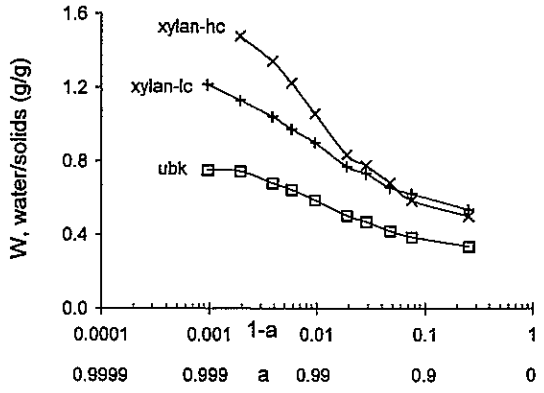

Fig. 6. The activity of the sorbed water for ubk and xylan samples. The moisture ratios of the samples are: ubk: 1.18, xylan-lc: 1.30, xylan-hc: 1.48 g/g

For pulp fibers the isothermal melting technique essentially measures the swelling of the gel phase in the high activity regime of about 0.900-0.999. Water at lower activities does not freeze and water at higher activities has a melting temperature too close to that of bulk water to be resolved with this technique. As expected the more highly charged xylan swells to a greater extent and contains more water at a lower activity than the xylan-lc sample. The higher amount of nonfreezing water in the xylan-lc sample is unexplained. This indicates the difficulty in comparing nonfreezing water data in systems with differing chemistry.

In order to confirm that the freezing bound water is related to the degree of swelling in hemicelluloses, the isothermal melting technique was applied to the original xylan-lc sample at MR = 2.3 g/g, and again after an additional drying-rewetting cycle at 50°C for 30 minutes. The original sample was obtained in the dry state. Under the mild drying conditions one expects no significant chemical changes to the xylan, and any changes in the activity curve to result from hornification. Hornification is the permanent loss of swelling which is known to occur when some polysaccharide gels are dried and rewetted. It is thought to be associated with the formation of hydrogen bonds between adjacent surfaces rich in hydroxyl groups of (Laivins, Scallan 1993). The results in Fig. 7 show that the twice dried sample has about 7% less water below the highest activity in

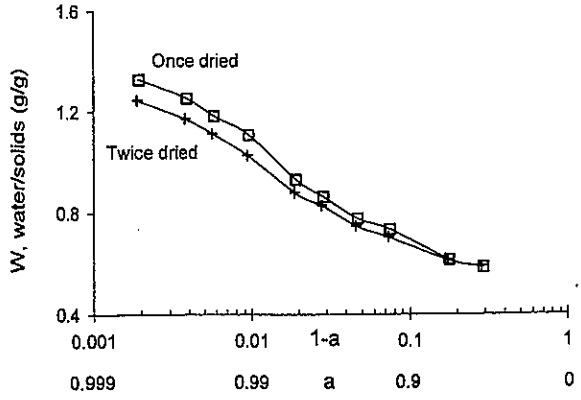

Fig. 7. The activity of sorbed water for xylan-lc after one and two drying cycles at MR = 2.3 ± 0.2 g/g.

this experiment (0.998, corresponding to -0.2°C). If one assumes that the formation of a hydrogen bond will involve the displacement of nonfreezing water then it may be concluded that the loss in swelling in this case involves the formation of comparatively few bonds.

Clearly, the same factors which cause the depression of the melting point of water in the hemicellulose gel samples also cause melting point depression in pulp fibers. If one chooses to view the amorphous gel regions as "microporous" or prefers to view the gel network as a solution is really a question of semantics. Expressing the melting temperature depression data as either pore radius or as activity is meant to illustrate these alternative views of the cell wall. However, pure water which is contained within sufficiently small pores which are outside the amorphous regions may also have a depressed melting temperature. This effect, based purely on geometry, is illustrated by the depression of the melting point of water in porous glass (Rennie, Clifford 1977).

The activity curve for water in a water/lignin mixture is shown in Fig. 8. In the first set of measurements it was observed that all the water in the sample had an activity less than 0.998. Since the lignin was prepared by precipitating at pH 2.5 and the DSC measurements were done in distilled water, near neutral pH, it is believed that the apparently high amount of freezing bound water is due to the dissolution of some low molecular weight substances. This was confirmed by washing the lignin thoroughly in distilled water and repeating the measurement. The results show that washing has removed a significant part, but not all of the hydrating material in the lignin sample.

In chemical pulp fibers it is known that residual lignin

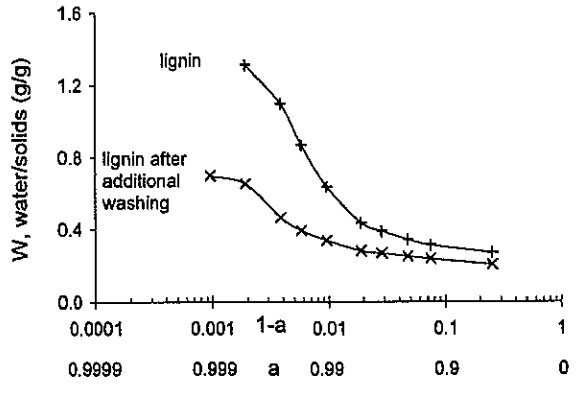

Fig. 8. The activity of water in a water/lignin mixture at MR =1.3 ± 0.1 g/g after precipitation at pH 2.5 and after additional washing in distilled water.

will slowly diffuse out of the cell wall (Favis, Goring 1984) and that this process is limited by steric effects and is dependent on e.g. pH and salt concentration (Lindström et al. 1978). It appears that the diffusion of macromolecules from the gel to the bulk phase can have a significant effect on the melting temperature depression curves for pulp fibers. This effect must be kept in mind because melting temperature depression caused by polymeric substances which are trapped in pores containing bulk water may be wrongly interpreted as coming from swelling or pore effects. Depression of melting temperature in the cell wall by the presence of soluble lignin, low molecular weight hemicelluloses or ions in the bulk phase are examples of solution effects.

Conclusions

The isothermal melting method is a reliable way to study the behavior of water in pulp fibers in a higher activity range than can be easily done with sorption isotherms. The technique is fairly simple and can provide information on the swelling and pore structure of pulp fibers. Isothermal melting measurements can be done at any moisture content at which freezing occurs and, because melting is carried out to completion, thermal delays are avoided.

Based on the existing evidence it is believed that in pulp fibers nonfreezing water is closely related to the number and type of adsorption sites. Both geometrical and solution effects can contribute to the melting temperature depression of water within the cell wall. The fact that the total bound water for a cotton sample is equal to the fiber saturation point measured with solute exclusion, indicates that the isothermal melting method is accurate. The measurements from a water/xylan mixture are consistent with the view the total bound water, consisting of both nonfreezing and melting temperature depressed fractions, is a measure of the swelling of the gel phase in heterogeneous hydrated polymer systems, such as wet pulp fibers. The experiments with lignin indicate that residual lignin which can leach out of the wall into the bulk phase can have a large impact on both nonfreezing and freezing bound water measurements.

A significant amount of water inside a never-dried ubk pulp has a melting temperature above -0.1°C. This implies that this water is in regions within the cell wall where pore and solution effects are negligible. A reasonable interpretation of this result, consistent with the accepted view of the cell wall structure, is that this water is located primarily between the gel-covered lamellae. Together with solute exclusion, the isothermal melting method provides a way to measure the swelling of pulp fibers in a more thorough way than has hitherto been done.

Acknowledgments

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