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SORPTION OF AQUEOUS AND NONAQUEOUS MEDIA BY WOOD AND CELLULOSE

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I. Introduction

Wood and its components, chiefly cellulose, as with any colloidal capillary-porous material change in size and shape when variations in temperature and relative humidity occur in the surrounding environment. Swelling and shrinkage will occur when aqueous or nonaqueous media are taken up or removed from the substance. These phenomena have a profound influence on the physical, mechanical, chemical, and electrical properties of wood and cellulose.

In this article, chiefly the take-up of aqueous and nonaqueous phases (in the liquid and vapor states) by wood and cellulose are considered although occasional reference is made to the take-up of gases as well. The relative merits and demerits of various experimental procedures for obtaining sorption data, the various sorption mechanisms, and a summary of important developments in sorption studies reported in the literature during the last decade are presented.

Also described in detail are the numerous mathematical models postulated by various research workers in an attempt to explain the sorption phenomena by polymers and the application of such models to correlate with and to evaluate other properties of wood and cellulose. Although all the theoretical models reported were not tested on wood and/or cellulose, they are reviewed critically since each one could be applied to any polymer including wood and cellulose.

II. Definitions of Terms

The terms related to sorption phenomena include (i) adsorption, (ii) absorption, (iii) sorption, (iv) desorption, (v) sorption isotherm, and (vi) sorption hysteresis. A survey of literature shows that the terms adsorption, absorption, and sorption are defined and used loosely.[1–8] All these terms in this article are defined in the following way.

The system which takes up the material is called the sorbent; that which is taken up is defined as the sorbate.

The take-up of *one or more molecular layers* by the sorbent from *a vapor phase* is defined as adsorption.

If the take-up of sorbate is *from a liquid phase* the phenomenon is termed absorption. When the exact nature of the mechanism involved is not known, the term sorption is used; in other words, the term sorption includes both adsorption and absorption. The term "sorption" was first introduced by McBain in 1909.[9]

The process of removing a sorbate from a sorbent is usually called desorption.

The relationship between the amount of material sorbed in terms of either the weight or volume of sorbate taken up per unit weight or unit volume of sorbent and the gas pressure or concentration of sorbate in solution at a fixed temperature is defined as the sorption isotherm. If the data are obtained during the removal of sorbate from the sorbent, then the relationship is called the desorption isotherm.

Experiments generally show[1] that the sorption and desorption isotherms for the same sample under the same conditions do not coincide. In other words, the amount of sorbate held by fibrous materials depends upon two factors: (i) equilibrium relative vapor pressure, and (ii) the direction from which equilibrium is approached. This phenomenon is known as sorption hysteresis and it was first observed in 1906 by Masson and Richards.[10]

The presence of air or other impurities can increase this effect.[11] Hysteresis may be a minimum when the system to be sorbed (if liquid) and the sorbent are degassed thoroughly by evacuation. This is particularly important at higher temperatures.[11]

According to some literature[1,12–16] the hysteresis loop is closed at the upper end. Recent data from sorption studies[17–19] show that this loop remains open at the upper end. Although Stamm[1] has commented on the difficulties of sorption measurements at 100% relative humidity, only further study will resolve this problem.

III. Experimental Procedures for the Measurement of Sorption

Sorption measurements have been made in a number of different ways. These include the following.

Volumetric method: letting a known weight of vapor into a system and determining the drop in vapor pressure to an equilibrium value from which the weight of the sorbed material can be calculated.[20–24]

Gravimetric methods: one approach is to suspend the sample from a calibrated helical spring[14,17,19,24–30] in a tube that can be evacuated and in which the atmosphere can be adjusted to produce a desired relative humidity. The gain or loss in weight of the sample due to changes in the environment is obtained from the change in length of the spring. Another is to determine the increase or decrease in weight of the sample in a room of controlled humidity and temperature.[31] When this experimental facility is not available, a desiccator technique is employed.[32–35] The source of sorbate (usually a saturated salt solution or an aqueous solution of sulfuric acid both of which will produce an atmosphere of the desired relative humidity) is kept in the lower part of a desiccator while the sample (in a container) is kept in the upper part. At suitable intervals, the sample is quickly taken out, weighed to determine the gain or loss in weight, and returned to the desiccator. This procedure is repeated until the weight of the sorbed or desorbed sample is constant. A modification of this technique is to suspend the sample from the left arm of a balance; this arm is sealed in a vessel whose atmosphere is adjusted to the desired relative humidity by a saturated salt solution. The weight of material sorbed at each moisture equilibrium condition can then be obtained directly by counterbalancing the other arm of the balance or by use of an electrobalance in which balance is obtained automatically.[36]

Water vapor sorption of single wool fibers was studied by a sorption vibroscope.[37] Several points of disagreement were observed between results obtained from this study and those from the vacuum technique. Of particular interest is that the uptake rates in the vibroscope were faster than those in the vacuum system, and a two-stage adsorption was observed up to about 30% regain in the vibroscope study but not above

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20% regain in the vacuum system. It was concluded that the vibroscope technique provides a convenient method of studying sorption and length swelling behavior of single fibers.

Labeling technique:[38–40] by introducing into a sorbate molecule a source of radioactivity. The course taken by such labeled molecules during sorption can be followed by a scintillation spectrometer. For convenience the radioactive material is diluted with a nonradioactive material to a known specific activity. The increase in radioactivity of the sorbent is then directly related to the amount of material sorbed.

All these methods have been employed in sorption studies of fibrous materials. The choice depends upon the condition under which a particular system is to be studied. Each method has its own advantages and disadvantages. For example, the volumetric method yields accurate data but involves correction factors and time-consuming calculations. Also, the basic assumptions involved in the calculation of the socalled "dead-space"[22] for the determination of sorption isotherms do not seem to agree with those used in the determination of density.[41] Recently Tarkow[5] has pointed out that the areas determined by the gas-adsorption (nitrogen) technique need not necessarily be the "proper" areas for characterizing a surface which sorbs polymers.

In the case of sorption studies using a room of controlled humidity or a desiccator employing different salt solutions, the isotherms can be obtained only for a very narrow temperature range. This procedure is also time consuming, unless several identical experimental setups are made, in which case it becomes uneconomical. This technique can be used only for water vapor sorption studies since drying the sample under vacuum is not always possible. Because predrying is not achieved, a longer period of time is needed to obtain equilibrium conditions. In the desiccator technique an error in weight is involved because of moisture loss while the sample is being weighed. Application of Wink's method[33] minimizes this error. Finally, for the desired reproducibility, extra care must be exercized and the sensitivity in the low vapor pressure region is poor.

The introduction of a radioactive source into the sorbate and the subsequent counting of the treated sample with a scintillation spectrometer is valuable for determining sorption isotherms when other reliable and rapid methods are not available, for example, sorption studies of polysaccharides by cellulose.[38–40] This method has several drawbacks:[38] the radioactive atom must not alter the sorption behavior of the labeled material relative to the unlabeled ones; complications such as selective sorption can occur; and it is extremely slow. According to Most,[38] equilibrium was not attained even after 240 hr of sorption.

Determination of sorption isotherms by suspending the sample at the end of a calibrated helical spring seems to be more versatile than the other methods. A typical experimental arrangement is shown in Figure 1. Measurements can be made on many samples simultaneously. The samples can be evacuated to a high degree of dryness. This facilitates the attainment of rapid equilibrium. Sorption measurements on any sorbate can be made at any temperature by immersing the sorption manifold in a temperature-controlled box. This method can be made very sensitive by the careful selection of the spring and the maximum weight of the sample. Note that the spring should be calibrated for any particular humidity and temperature.

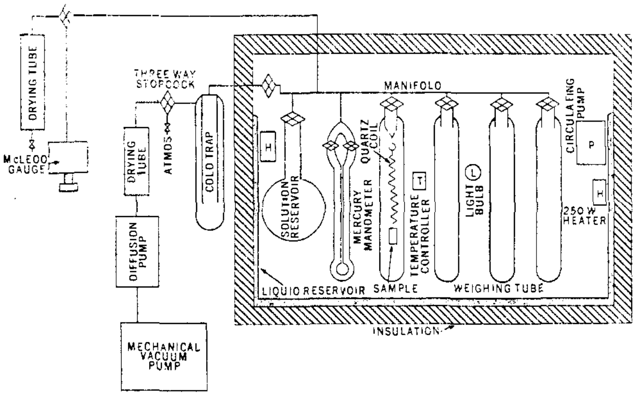

Figure 1. Sorption system.

To minimize the errors due to nonuniformity in humidity or temperature, the entire system should be immersed in a bath, preferably a liquid one. Partial immersion[42] of the system in the bath and the exposure of the remaining part of the system to room condition yield inaccurate results. There is one experimental difficulty common to all the methods described, namely the collection of data at and near 100% relative humidity.

Absorption studies of several sorbates also have been made[43] by actually soaking the fibrous material in solution and then letting the samples undergo desorption and adsorption through a range of relative humidity values. In such cases the samples were first vacuum dried at temperatures slightly above that of the room. For such samples this type of drying was found to be more suitable than oven drying.[43]

IV. Mechanisms of Sorption and Hysteresis

Several suggestions are put forward in the literature as to possible mechanisms by which water or water vapor is taken up by the cell walls in wood and other fibrous materials. These include:[3] the surface adsorption theory, the capillary condensation theory, the solid solution theory, and two very recent mechanisms, *viz.* a two-phase mechanism[44] and a mechanism based on pore-size distribution.[45]

According to the surface adsorption mechanism, the large internal surface of the fibrous material, wood or cellulose, contains polar groups, particularly hydroxyl groups. These surfaces belong to those of the subunits of molecular segments or those surrounding accessible portions of the material. The initial take-up of water vapor is supposed to be distributed in a monomolecular fashion. At higher humidities polymolecular adsorption occurs. Note that this theory, however, does not adequately account for the rapid increase in moisture content at high *relative* vapor pressures.[3]

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Table I

Radii and Volumes of Pores in Swollen Spruce[45]

Radius of the capillary, Å	16–19.5	19.5–33	33–76	76–200	200–1045	1045–4200
Volume of the capillaries, cm^3/g of wood	0.027	0.026	0.008	0.004	0.002	0.015

The capillary condensation theory[3] explains the sorption phenomenon occurring only at high relative humidities. Most of the capillary condensation taking place within the cell walls must be confined to a relative vapor pressure ranging from 0.90 to 0.995. According to this mechanism, the vapor pressure of water in a capillary depends on the radius of the capillary and decreases with decreasing radius. Using the Kelvin equation[1]

$$\ln\left(\frac{p_0}{p}\right) = \frac{2\sigma M}{\rho r R T} \tag{1}$$

where p_0/p is the relative vapor pressure, σ the surface tension of the liquid, M the molecular weight of the liquid, r the radius of the capillary, ρ the density of the liquid, R the gas constant, and T the absolute temperature. Stamm[1] has calculated the capillary sizes that will fill with water (from the vapor phase) when the water is in equilibrium with various relative vapor pressures ranging between 0.9000 and 0.9999.

The swelling theory[3] was introduced to explain the sorption mechanism of synthetic fibers which are highly accessible. This mechanism assumes that the take-up of water occurs essentially in the disordered region rich in hydroxyl groups (these are capable of forming hydrogen bonds with water molecules). This concept explains the sorption behavior over a wide range of relative humidities.

Table I gives the distribution of radii of the micro- and submicroscopic volumes in spruce swollen in water.[45,46] This distribution was obtained after an initial desorption with benzene vapor. These results show that the finest capillaries with a radius up to 33 Å occupy the largest volume and contribute most to the internal surface of wood. The pores may be divided into three groups: supercapillaries with radii in excess of 0.25 mm, sometimes found in wood of the annular vessel species; microcapillaries whose radii range between 0.25 mm and 0.10 μ encompassing all the voids between the cells; and microcapillaries with a radius less than 0.1 μ which contribute to the formation of the internal surface of wood. The submicroscopic capillaries with a radius a few times larger than that of the water molecule play an important role in the adsorption process.

On the basis of these three types of pores, and recognizing that the properties of wood change during adsorption, the following mechanism of sorption and swelling of wood was proposed.[45]

At low partial pressures when the dry surface of wood comes into contact with water molecules, an intensive adsorption starts. More water molecules penetrate the microscopic capillaries of wood and very soon the surface of the wood is covered with pellicular water. The formation of pellicular water depends upon the physicochemical properties of the sorbent and sorbate and also possibly on the surrounding medium. When a few layers of water molecules have formed on the open surface, the water diffuses into the internal surfaces of wood formed by microcapillaries and by submicroscopic capillaries. Following Timofeeva,[47] Chudina[45] assumed that small groups of water molecules break away at the entrance of the submicroscopic capillaries of wood and these water molecules penetrate the capillaries.

Subsequently the micro- and larger capillaries are filled with water molecules. Furthermore, there is a considerably reduced effect of heat of adsorption which accompanies the adsorption by the wood of the water subsequently adsorbed. Generally speaking, this heat effect approaches zero after the formation of three to five layers of water molecules on the internal surface of the wood. When this heat effect ceases, the actual adsorption ends and the remaining part of the hygroscopic water is incorporated by the wood by capillary condensation.

The radii of the capillaries filled with water during the entire process depends upon the temperature and vapor pressure of the surrounding air. As the vapor pressure increases, the radius increases. According to Chudina,[45] when the relative humidity of the air reaches 100%, the radius of a capillary in which condensation of water vapor is possible at room temperature is 0.1 μ. Note that, according to Stamm,[1] the pore radius at 99% relative vapor pressure is 0.106 μ and that at 99.99% it is 10.6 μ.

From his sorption study on wood by vapor and liquid (Table II) Christensen[44] suggested the following mechanism by which water or water vapor is sorbed by wood cell walls. His experiments showed the following.

The faster uptake of liquid than of vapor suggested that in addition to the molecular process of water transport and swelling within the solid phase, interfacial phenomena play an important role in the adsorption process.

The sorption of both liquid and vapor depends strongly on the initial treatment of the sample. The rate of uptake of liquid by wood initially dry (or conditioned to a low vapor pressure) was insensitive to previous conditioning but strongly depends on the thickness of the cell wall.

Rates of sorption of both liquid and vapor were found to be largely independent of the material thickness under those conditions in which they are strongly sensitive to the ratio of initial and final relative vapor pressures.

Considering these results, Christensen[44] believes that the uptake of both liquid and vapor involves two consecutive processes.

In the first stage the liquid or the vapor penetrates the cell wall by a number of discrete pathways, such as preexisting cell wall capillaries or void spaces in the fiber. The rate in this

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(46) P. P. Erin'sh, "The Effect of the Rate of Swelling on the Capillary Structure of Spruce Wood and Its Components," Kand Diss. (Candidate's Dissertation), Riga, 1962.

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Table II

Rates of Sorption and Swelling (on Klinki Pine) Characterized by the Reciprocal of the Time Taken to Reach Half the Change in Sorption or Swelling between the Initial and Final Equilibrium Conditions[44]

	Sorption of vapor		*Swelling in liquid* ($p_t = 1$)		
	Water	*Methanol*	*Water*	*Methanol*	*Ethanol*
$p_i = 0$	2×10^{-2}	1×10^{-3}	1.5	1×10^{-1}	1.5×10^{-3}
$p_i/p_t = 0.7$	6×10^{-4}	1×10^{-4}	1	1.5×10^{-3}	2×10^{-5}
$p_i/p_t = 0.8$	2.5×10^{-4}	2.5×10^{-5}	2×10^{-1}	3×10^{-4}	3×10^{-6}
$p_i/p_t = 0.9$	3×10^{-5}	...	5×10^{-2}	2.5×10^{-5}	...

stage strongly depends on the cell wall thickness but not on the initial condition of the samples.

The second stage consists of molecular migration into the intervening solid regions, which are governed by the true swelling of the solid phase. In this second process, occurring in a large number of regions of the cell wall simultaneously, the rate does not depend on the thickness of the cell wall but rather on the initial vapor pressure and also on whether it is vapor or liquid which is being introduced at the interface.

There is no generally accepted explanation for the sorption-hysteresis effect. The literature[3,48] shows varying and contradictory explanations for the cause of hysteresis. Zsigmondy[49] believed that the difference in the values of sorption and desorption is caused by the wetting properties of the capillary walls. Since no capillary condensation exists at low vapor pressures and consequently no wetting is possible, this explanation[50] is not completely valid.[48] The hypothesis that hydroxyl groups are responsible for hysteresis in cotton fibers leads to the conclusion[48] that the hydroxyl groups satisfying each other are not available for adsorption of water. According to Barkas[51,52] the principal cause of hysteresis in wood is its plasticity. Another explanation[3] is that the adsorbed molecules of water cause swelling of the hemicelluloses when surfaces of dry cellulose come into equilibrium with atmospheres of increasing humidity. This swelling breaks secondary bonds between molecules and molecular segments of hemicelluloses. With an increase in vapor pressure, the breaking of bonds increases the number of hydroxyl groups able to act as strong sorption sites. Under such conditions if desorption occurs the network tends to contract. This contraction is delayed by the persistence of bound water on the new sorption centers formed by adsorption. Consequently, a higher moisture content is obtained at a given relative vapor pressure on desorption.

V. Negative Swelling Observed in Fibers and Wood

Hermans[41] observed that the density of fibers determined by flotation method[41] first increases with moisture, then goes through a maximum, and finally decreases steadily. Originally this phenomenon was interpreted as "compression of bound water"[41] which was later on found to be "superfluous."[53] The reduction in the total volume of a system by sorption of a liquid was found to occur in other fibers, such as wool.[53] A very careful sorption study[45] on Siberian larch showed that there was a contraction in swelling during the initial period of sorption (between 15 and 50 min). This was observed in both tangential and radial directions of wood, although the contraction was greater in the tangential direction (0.017%).

Several explanations were put forward in an attempt to explain this negative swelling occurring during the initial stage of sorption. Although the compression hypothesis has been criticized,[53] there may be a volume contraction due to electrostriction of sorbate molecules around charged groups in fibers. Another explanation is based on filling "pores" in fibers.[53]

The experimental observations can be more satisfactorily accounted on the basis of the volume relations borrowed from the packing of spheres.[41] The initial specific volume of the dry fiber may be regarded as the volume occupied by the cellulose molecules and a fractional empty space. According to the volume relations based on the packing of spheres, if water molecules are inserted between and packed among the cellulose molecular segments, part of the empty space will be occupied by water and the increase in volume of the fiber will be generally less than that computed additively from the initial volumes of cellulose and water separately. Consequently, macroscopically a contraction is observed. The magnitude of this negative swelling depends on the shape and dimensions and molecular arrangements in the system.

In fibers, the contraction is significant up to 4% regain, and the water is bound with an apparent density of 1.6 which is greater than that of fiber substance.[41] Beyond 4% regain the apparent density of bound water decreases very rapidly and approaches asymptotically the normal value, namely unity.

The negative swelling observed in the early stage of moisture sorption by wood was explained on the basis of the formation of monomolecular layers of water in the submicroscopic capillaries.[45] Wood and cellulose are polymers similar to glass (noncrystalline) with hard linear chains in a friable packing. The distance between the links of the adjacent submicrocapillary permit the water molecules to penetrate between them and attract the walls of the capillary to itself. The energy of this attraction, which is equal to the excess of energy of the capillary walls acting on the water molecules, causes an elastic displacement of the molecular segments of cellulose. This is possible since the transverse bonds between adjacent hydrogen bonds are weaker than the chemical valence bonds in the water molecules. The result of this drawing together of the submicrocapillary walls and the water molecules is a general slight decrease of the wood dimensions across the grain (Figure 2).[45] The broken lines in Figure 2 show the position of the micromolecules of the cellulose before penetration of water molecules between them. The solid lines indicate the displaced positions of the molecular segment after their attrac-

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(48) F. Kollmann, *Colloq. Int. Centre Nat. Rech. Sci.* (Paris), No. 160, 187 (1967).

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(51) W. W. Barkas, *Trans. Faraday Soc.*, 35, 388 (1939); 36, 824 (1940); 38, 194, 447 (1942).

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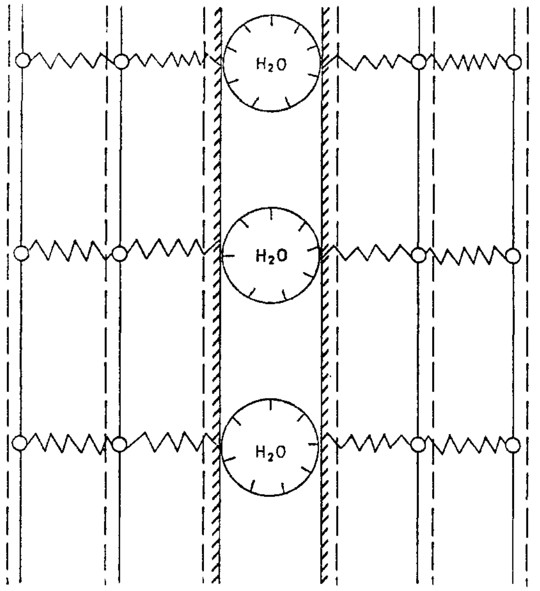

Figure 2. A schematic representation of interaction between capillary walls and water molecules occurring at a monomolecular layer.[45]

tion to the penetrated water molecules. The transverse bonds between the micromolecules of cellulose are represented in the form of elastic springs. As more water molecules are sorbed the microfibrils expand and positive swelling occurs.

The contraction volume V_c accompanying sorption has been calculated as[53]

$$V_c = \left(\frac{W_1 - W_2}{W_2 d}\right) - (V - V_d) \qquad (2)$$

where V_c is the contraction volume (cm^3/g of dry fiber), W_1 the weight of sorbed fiber, W_2 the weight of dry fiber, d the density of sorbate, V the volume of fiber containing sorbate/g of dry fiber, and V_d the specific volume of the dry fiber.

VI. Effect of Different Factors on Sorption by Wood and Cellulose

A number of sorption studies of theoretical and practical interest has been reported in recent years. These include studies of both aqueous and nonaqueous sorption by wood and cellulose.

A. EFFECT OF EXTRACTIVES ON WATER VAPOR SORPTION BY WOOD

The effect of removable extractives (3–17% by weight) of nine tropical wood species on water-vapor sorption relationships has been investigated.[19] Samples were Soxhlet-extracted successively using 2:1 benzene-alcohol (95%), 95% alcohol, and distilled water. The results can be summarized as follows: the desorption isotherms show that the fiber saturation points of unextracted species (20.5–32.8% by weight) were increased after extraction (30.4–38.0% by weight). Extracted and unextracted samples had approximately the same sorption–desorption data below 60% relative humidity, which means that the basic mechanism of sorption involved is the same in both cases. Wherever polymolecular sorption dominated, the total sorption showed similar relationships except in the case of essentially extractive free wood for which the total sorption could be expected to reflect the availability of molecular sorption sites and hence show significant variation in the crystalline content, cell wall density, or chemical composition.

B. EFFECT OF RATES OF WATER AND ALCOHOL SORPTION BY WOOD AND WOOD CONSTITUENTS

Studies[44,54,55] of water vapor sorption by thin specimens of vacuum-dried wood, wood fillers, hemicellulose, and regenerated cellulose showed that sorption rates are determined by a mechanism which differs from that of diffusion in its dependence on the conditions of sorption (the average diffusion coefficient tends to decrease as the specific gravity increases in both longitudinal and radial directions and in both sorption and desorption processes).[56] This conclusion was based on the following experimental results:[44] below a limiting thickness, the rate of sorption was independent of thickness; for moisture increments of a given size the sorption rate was much lower at higher initial moisture contents, whereas the diffusion coefficient is greater at higher moisture contents; large moisture increments were completed much faster than small ones for the same final moisture content. The hypothesis[44] that the rate of sorption by these materials was limited by relatively slow molecular rearrangements within the swelling substance was inadequate to explain the behavior observed when liquid replaced vapor as the external phase. A study[44] was made on klinki pine (*Araucaria hunsteinii* K. Schum.) with deaerated water, methanol, and ethanol. The liquids were brought into intimate contact with the cell wall surfaces (2–3 mm long) for a very short period of time (between 0.02 and 0.2 sec). The transverse swelling was recorded photographically at up to 8000 exposures/min. Some of the results are given in Table II. The observations[44] were that the rates of swelling in liquid were several orders of magnitude faster than that of vapor, the swelling rate in alcohol was less than that in water, and, below a relative vapor pressure value of 0.7, the swelling rate in water depended strongly on cell wall thickness. Elaboration of these results led to a new hypothesis[44] by which the uptake of vapor and liquid by wood is explained.

Water-vapor sorption studies[57] on isolated wood components, *viz.* wood cellulose, hemicellulose, and lignin, revealed that the general isotherms for all these components were similar and that each component contributed approximately 47, 37, and 16%, respectively, of the total sorption. Lignin prepared differently showed differences in isotherms, possibly due to variation in specific gravity and other changes such as oxidation and condensation occurring during isolation.

C. DEPENDENCE OF MOLECULAR WEIGHT OF POLYMERS ON SORPTION BY WOOD SURFACES

The sorption data[58] of polyvinyl acetate (PVAc) from a benzene solution onto alcohol–benzene–extracted red lauan wood

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(54) T. Sadoh and G. N. Christensen, *Aust. J. Appl. Sci.*, 15, 297 (1964).

(55) G. N. Christensen, "Humidity and Moisture," Vol. 4, A. Wexler, Ed., Reinhold, New York, N. Y., 1965, p 279.

(56) T. Yokota and K. Goto, *Bull. Govt. Forest Exp. Sta.*, No. 198, 201 (1967).

(57) K. E. Kelsey and G. N. Christensen, *Aust. J. Appl. Sci.*, 10, 269 (1959).

(58) M. Taniguchi, K. Nakato, and N. Shiraishi, *J. Jap. Wood Res. Soc.*, 14, 227 (1968).

(radical section 100 μ thick) agreed well with the Langmuir type of sorption and showed a maximum of sorption of branched PVAc at a particular degree of polymerization ($P = 3200$). It was supposed that the absorption occurred only on the surface and the reason for maximum value of sorption at $P = 3200$ was attributed to the variation of pore-size distribution. In another study[59] under equilibrium conditions, poly(methyl methacrylate) (PMMA) was preferentially sorbed by wood from a polystyrene–PMMA mixture in trichlorobenzene solution, and PVAc was also preferentially adsorbed by wood from PMMA–PVAc mixture in trichloroethylene solution.[5] This characteristic selective adsorption resulted from the dipole moments of these polymers.

In studies of this type[60] the solvent also should be taken into consideration when the true adsorption of polymers onto the porous systems from dilute polymer solutions is evaluated. The true adsorption value of the polymer (g/g) is given by[60]

$$u = s + \frac{wc}{1 - c} \tag{3}$$

where

$$s = \frac{M_0(c_0 - c)}{G(1 - c)}$$

s = apparent adsorption value of polymer (g/g); M_0 = weight of solution (g), C_0 = initial concentration (g/g), c = equilibrium concentration of polymer solution (g/g), G = weight of adsorbent (g), and w = weight of solvent sorbed by adsorbent (g/g). The schematic representation of sorption of solvent into porous adsorbent and a comparison between the true and apparent adsorption of PVA from aqueous solution on vacuum-dried red lauan wood meal are given in Figures 3 and 4.

D. EFFECT OF TEMPERATURE ON THE WATER VAPOR SORPTION OF WOOD AND CELLULOSE

Sorption data on 12 different North American wood species at 3, 10, and 70°F showed[31] that the isotherms at 10°F have the same slope as those at 70°F. According to Hedlin,[31] the moisture contents at 10°F and at about 99% relative humidity (relative to ice) were much lower than those reached at about the same relative humidity at 70°F. A sorption study[61] of kraft paper between 30 and 95% relative humidity at four specific temperatures (20, 5, −5, and −20°) showed (Figure 5) a maximum in moisture sorption in the neighborhood of 0 to 5° and also the difficulty in extrapolating the data obtained at higher temperatures to sub-zero temperature, especially at high relative humidities. This anomaly, that the moisture sorption at a given relative humidity, below 0°, is lower than that at room temperature, was observed earlier in textile materials.[62]

Using a modified Clausius–Clapeyron equation and assuming that freezing and nonfreezing water exist in a textile material below 0°,[63] Whitwell and Willmer[64] developed equa-

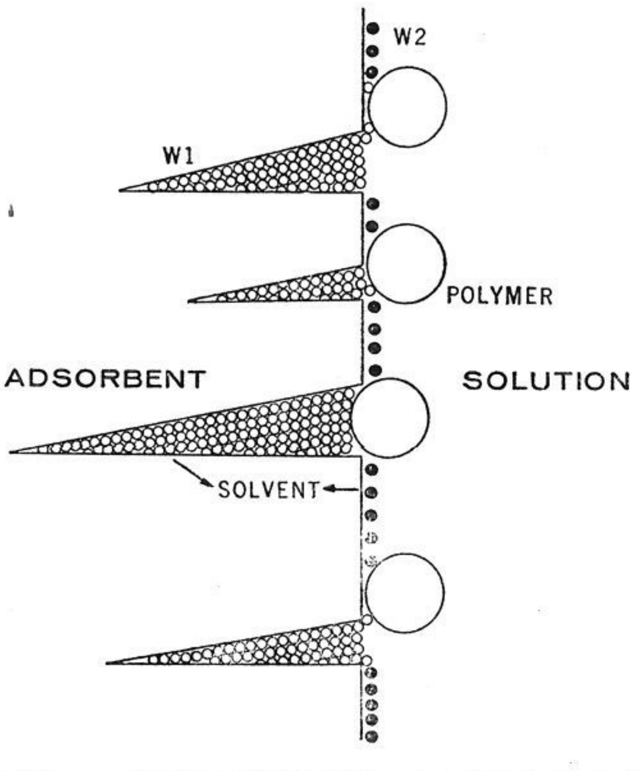

Figure 3. Representation of sorption of solvent to porous adsorbent.[60]

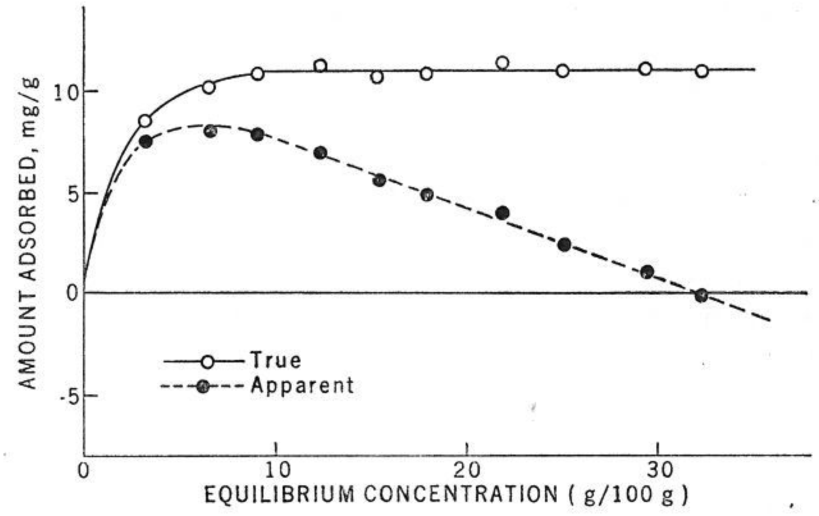

Figure 4. Comparison between true and apparent adsorption isotherm of PVA from aqueous solution on vacuum-dried hinoki wood meal.[60]

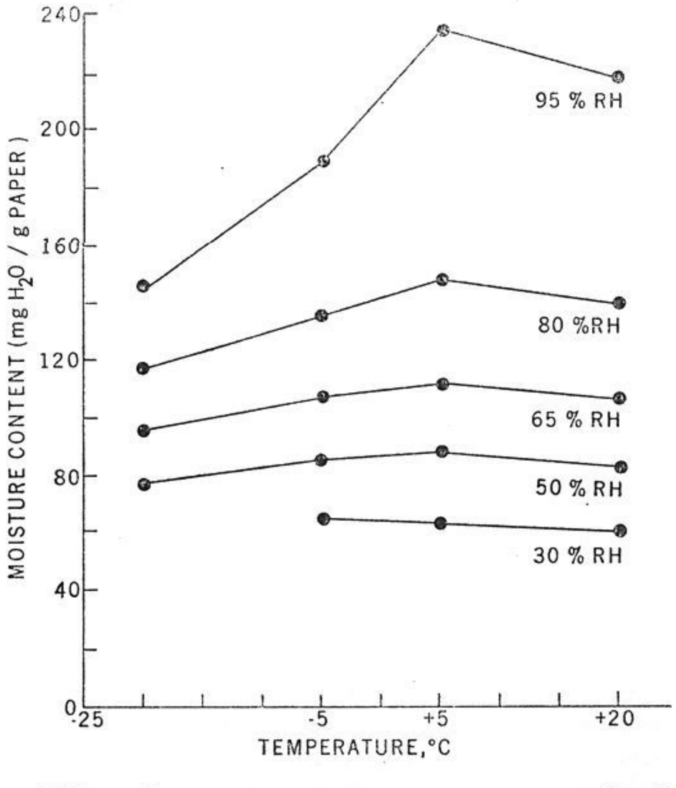

Figure 5. Effect of temperature on water vapor sorption by kraft paper.[61]

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[59] N. Shiraishi, Y. Ishimaru, N. Nakato, and T. Yokota, *J. Jap. Wood Res. Soc.*, **14**, 347 (1968).

[60] N. Shiraishi, Y. Ishimaru, N. Nakato, and T. Yokota, *ibid.*, **15**, 20 (1969).

[61] R. T. Skogman and C. E. Scheie, *Tappi*, 52, 489 (1969).

[62] R. C. Darling and H. S. Belding, *Ind. Eng. Chem.*, **38**, 524 (1946).

[63] F. C. Magne, H. J. Portas, and H. A. Wakeham, *J. Amer. Chem. Soc.*, **69**, 1896 (1947).

[64] J. C. Whitwell and D. B. Willmer, *Text. Res. J.*, **17**, 664 (1947).

tions for various isosteres to accommodate the variation in slope as a result of the freezing condition. Their calculations do not allow for the experimentally observed anomaly in sorption at a temperature below freezing.

An analysis of the experimental procedures and results[61,62] leaves little doubt regarding the existence of this anomaly at low temperatures. Isostere equations[64] based on a modified Clausius–Clapeyron equation accounted only for the phase change of water at the freezing point. It is conceivable that a secondary transition (phase change) could occur in cellulose or the cellulose–water system at low temperatures which could cause the reversal in slope at low temperatures.

E. EFFECT OF AMMONIA TREATMENT ON SORPTION CHARACTERISTICS OF WOOD

Following Stamm's discovery,[65] several articles[66–69] have been published stating that ammonia is a potential plasticizer of wood and would be commercially valuable. A recent study[30] on ammonia-treated yellow birch (*Betula Alleghaniensis* Britton) was reported in great detail. The first sorption isotherm at 25° differed considerably from the generally known isotherm for water on wood. This was probably due to the intrusion of ammonia into the fractional crystalline content in wood. Although subsequent sorption and desorption isotherms were similar to the wood–water system, a larger sorption for ammonia-treated wood was observed. Comparison of sorption hysteresis of the wood–ammonia and wood–water systems (Figure 6) showed that, during the first desorption–sorption cycle, the hysteresis of the wood–ammonia system was much greater than that of the wood–water system. This difference decreased for subsequent cycles.

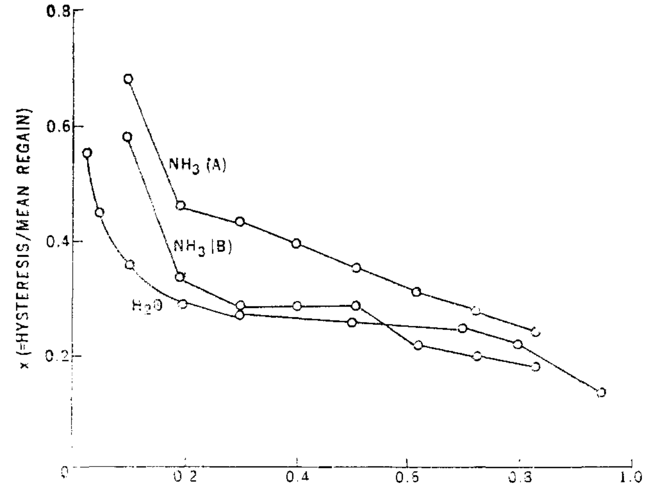

Figure 6. Comparison of hysteresis during ammonia desorption–adsorption cycles with similar data for water sorption.[30]

F. EFFECT OF SALT TREATMENT ON SORPTION–DESORPTION CHARACTERISTICS OF WOOD

The use of chemically impregnated wood as a building material has significantly increased in recent years. Such chemical impregnation involves the use of inorganic salts, and the treatment affects the strength properties, hygroscopicity, and dimensional stabilization of wood. A study was made[43] of water-vapor sorption and desorption on ponderosa pine and red oak with varying levels of salt retention. Phosphate treatment showed no significant change in equilibrium moisture content. The increased moisture content observed for borax and boric acid treatments was not a permanent effect owing to the nonhygroscopic nature of these salts. Treatment with either sodium chloride, zinc chloride, or ammonium sulfate resulted in a considerable increase in equilibrium moisture content for the entire range of relative humidity. This effect was greater in pine than in oak. The equilibrium moisture content (in per cent on weight basis) for any species of wood when treated with any of these chemicals could be obtained from[43]

$$M = 100(A + Bx) \qquad (4)$$

where A is the equilibrium moisture content of untreated wood of the species involved at the atmospheric condition being considered, B the slope of regression line, and x the salt–wood weight ratio. Volumetric swelling (swelling based upon the untreated dry volume of the specimen) increased with these treatments. This swelling effect was greater in the case of salts which are hygroscopic.

To elucidate the mechanism of graft copolymerization of cellulose in the presence of a ceric salt initiator, cellulose was treated with an aqueous solution of the ceric salt.[70] The ceric ion is consumed in a reaction which is approximately first order in both the oxidation of and absorption on cellulose. The ions so adsorbed were so strongly bonded that washing with water, dilute acid, or alkali could not desorb the salt. It was concluded that, because of its stability, the contribution of the ceric ion to the graft polymerization was small.[70]

Wood samples (80 cm long and 15 cm in diameter) containing 80% m.c. were impregnated with a solution of polyethylene glycol (35% by weight).[71] These samples were subjected to various relative humidities between 20 and 100%. The treated samples sorbed a higher moisture content and were more sensitive to rapid humidity changes than the untreated samples. This resulted from the replacement of polyethylene glycol by water at the surface.

G. INFLUENCE OF MECHANICAL STRESS ON THE SORPTION EQUILIBRIUM OF CELLULOSE

The sorption change in cellulose under stress and its contribution to stress distribution in paper rolls are of practical significance. Limited studies in this direction (both theoretical and experimental) have been made.[51,52,72,73] According to the concept of elasticity of a gel,[51] in the case of an uniaxial stress exerted on a rectangular body, the change of moisture con-

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(65) A. J. Stamm, *Forest Prod. J.*, **5**, 413 (1955).

(66) C. Schuersch, *Ind. Eng. Chem.*, **55**, 39 (1963).

(67) C. Schuersch, *Forest Prod. J.*, **14**, 377 (1964).

(68) C. Schuersch, M. Burdick, and M. Mahdalik, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 105 (1966).

(69) R. E. Pentoney, *ibid.*, **5**, 105 (1966).

(70) O. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Polym. Sci., Part A-1*, **6**, 1489 (1968).

(71) U. Tamburini, *Ric. Sci.*, **38**, 1194 (1968).

(72) W. W. Barkas, *Nature*, **162**, 32 (1948).

(73) J. Kubat and L. Nyborg, *Sv. Papperstidn.*, **68**, 698 (1965).

tent of the gel, dq, due to an infinitesimal increase of the stress, dσ, is given by[73]

$$\left[\frac{\mathrm{d}q}{\mathrm{d}\sigma_x}\right]_{\mathrm{p}} = \left[\frac{1+q}{\rho_{\mathrm{m}}vp_0}\right]\frac{1}{x}\left[\frac{\mathrm{d}x}{\mathrm{d}(p/p_0)}\right]_{\sigma_x} \quad (5)$$

where q is the ratio between the weight of water and the weight of dry substance, x the dimension of a rectangular block of a swollen gel, σ_x the external force acting in the direction of x, ρ_{m} the density of the gel in the swollen state, v the specific volume of vapor, p_0 the saturation vapor pressure, and p the vapor pressure. The application of this equation to cellulose was rather limited[73] since this theory was developed purely for elastic deformations, whereas in the case of cellulose, plastic flow undoubtedly occurs.[73]

H. SORPTION OF HEMICELLULOSES AND OTHER POLYSACCHARIDES BY CELLULOSE

The sorption of hemicelluloses and other polysaccharides such as gums (used as beater adhesives) by cellulose was studied by an absorption technique using a radioactive material such as carbon (^{14}C) and tritium.[8,37–39] The sorption of polysaccharides is both important and interesting in pulp and paper technology since it helps to increase yield, it controls residual hemicelluloses in the manufacture of dissolving pulps, and it produces certain desirable characteristics in various grades of paper board.

Several studies[37–39] of sorption of polysaccharides (slash-pine hemicelluloses, modified locust-bean gum, spruce glucomannan, and modified birch xylan) by cellulosic materials using the labeling technique have been reported. These studies include the measurements of sorption as a function of time, initial concentration of the polysaccharides in solution, temperature, consistency, specific surface area, pH, and rate of agitation. Although much of the sorption occurred within the first 24 hr, equilibrium was not achieved even after 240 hr. An increase in the initial concentration, temperature, consistency, or specific surface area resulted in increased sorption, while an increase in pH reduced sorption. The rate of agitation had no effect on sorption.

Sorption and desorption of birch and pine xylans on cellulose fibers at a constant pH were studied[74] using a continuous-flow reactor. The structure of the xylan affected the sorption significantly. A complete removal of the uronic acids in birch xylan doubled the sorption. The data obtained from this study showed that sorption was monomolecular in nature.

The mechanism of sorption of polysaccharides by fibers was described as follows:[37] when cellulose fibers are introduced into a solution of hemicellulose, sorption occurs at a rapid rate. Initially hemicellulose chains are deposited onto the "bare" cellulose surface. According to Simha, flexible macromolecules are sorbed on substrates through molecular chains. The sorbed segments are interconnected through unsorbed molecular "bridges" extending into the solution. It is very likely that such an orientation occurs since hemicelluloses have numerous hydrogen-bonding hydroxyl groups. Once the cellulose surface is covered by hemicellulose units, a second type of sorption occurs, namely, hemicellulose-on-sorbed hemicellulose. This type of sorption decreases when a greater quantity of hemicellulose is sorbed. Desorption occurs when the bonds holding a molecule or a molecular segment break.

I. EFFECT OF CHEMICAL MODIFICATION ON SORPTION OF CELLULOSE AND WOOD

Treatment[75] of cotton linters and ramie fibers with caustic soda of various concentrations in water and testing for moisture sorption at 0 and 20° showed that maximum sorption of water occurs at complete mercerization, *i.e.*, treatment with about 4 *N* sodium hydroxide for ramie and between 4 and 7 *N* for cotton. Beyond these values of concentrations no change in sorption at 0 and 20° was observed.

Bleached cotton fibers were cross-linked with formaldehyde by various processes,[76] in the presence of hydrogen chloride as catalyst. Caustic sorption on these samples were then determined in terms of alkali centrifuge values, defined as the amount of caustic solution that was sorbed. The alkalinity of the centrifuged samples was determined by titration. The alkali centrifuge values of the cross-linked cotton from vapor-phase reactions decreased rapidly with increasing formaldehyde content. The sorptivity was reduced by 20% when the samples contained 0.1% formaldehyde. Those values of cotton cross-linked in aqueous media increased to a maximum value at about 0.2% of formaldehyde. This study also confirmed[76] the fact that cotton preferentially sorbed sodium hydroxide, which indicates the degree of available hydroxyl groups within disordered and ordered regions in cellulose. The moisture sorptions of the original cross-linked samples were found to depend on the method of cross-linking and decreased or increased with formaldehyde content.

The hygroscopicity of cellulose modified with potassium metaperiodate increased with the degree of periodate oxidation.[77] Subsequent reduction of cellulose with sodium borohydride resulted in a decrease of regain to a value approximately equal to that of the original material.

The moisture sorption of cellulose is changed when progressive acetylation of the hydroxyl groups occurs.[78] When the noncrystalline regions are completely acetylated the water sorption is a minimum. The effect of sorption is demonstrated in Figure 7. Laffend and Swenson[79] found that the sorption of acetyl glucomannan by cellulose markedly affects the properties of this polymer and its pulping characteristics. The removal of glucomannan acetyl groups led to decreased water solubility, a higher rate of sorption, and an earlier mass equilibrium. The specific sorption of acetylated glucomannan approached a maximum (7.5%) while the sorption of deacetylated glucomannan was a function of the amount added.

An excellent linear relationship was found[5] between the absorption of polyvinyl acetate by carbon tetrachloride treated wood (from carbon tetrachloride solution) (mg/g of wood) and the computed specific surface area of the exposed end-grain of the wood substance (cm^2/g). The reactivity between the two components, *viz.* the exposed wood substance and lumen walls, was very different (the reactivity expressed in terms of the amount of polymer sorbed per unit area of wood substance was much greater than that of the lumen walls). It was

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(74) J. A. Hansson and N. Hartler, *Sv. Papperstidn.*, **72**, 521 (1969).

(75) J. O. Warwicker, *J. Polym. Sci., Part A-1*, **5**, 2579 (1967).

(76) E. Honold, S. P. Rowland, and J. N. Grant, *Text. Res. J.*, **39**, 1023 (1969).

(77) P. J. Kangle and G. M. Nabar, *J. Appl. Polym. Sci.*, **12**, 2533 (1968).

(78) L. E. Herdle and W. H. Griggs, *Tappi*, **48**, 103A (1965).

(79) K. B. Laffend and H. A. Swenson, *ibid.*, **51**, 118 (1968).

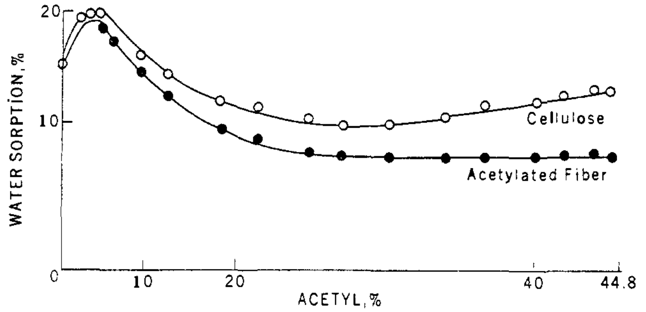

Figure 7a. Effect of fibrous acetylation on moisture sorption at 95% relative humidity and 40°.[78]

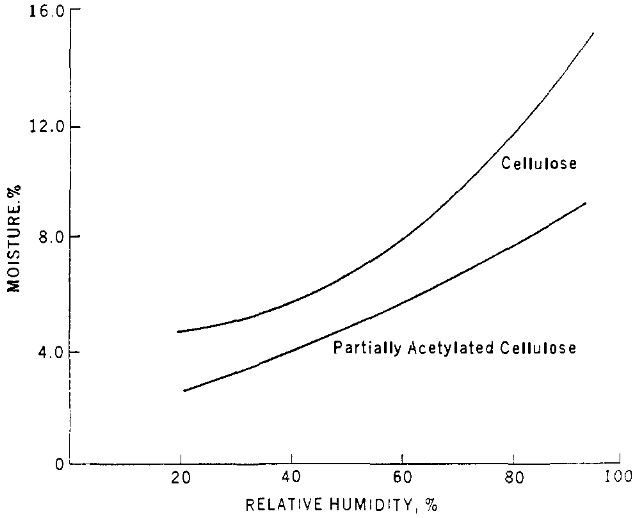

Figure 7b. Moisture sorption of paper (hemlock kraft pulp containing 21% acetyl).[78]

concluded[5] that the area available for sorption is composed of these two components; the actual composition varies from one wood to another.

J. EFFECT OF PREVIOUS HISTORY ON SORPTION BY WOOD

A very limited study[80,81] showed that the rate of sorption of water by wood strongly depends on the previous history of the samples.

Many fibrous materials such as wood and cellulose behave differently during sorption and desorption processes (hysteresis).[1] The equilibrium moisture content in a given sample at a given relative vapor pressure depends on the number and duration of the intermediate equilibrium steps by which it is reached. The dependence of previous history[80] on sorption was demonstrated on vacuum-dried samples. At room temperature, the quantity of water retained by a sample after vacuum drying varied according to the period of previous exposure of the sample to vapor. One report[80] showed that the effect of the conditioning period on the retention of water by the samples after vacuum drying is linear up to 1000 hr (Figure 8).

One of the implications of these studies is that a state of complete equilibrium in wood may be a relatively rare occurrence. In order to obtain meaningful and reproducible sorption data for materials such as wood and cellulose and possibly other swelling polymers in general, extreme care must be taken with the previous history of the sample.[80,81]

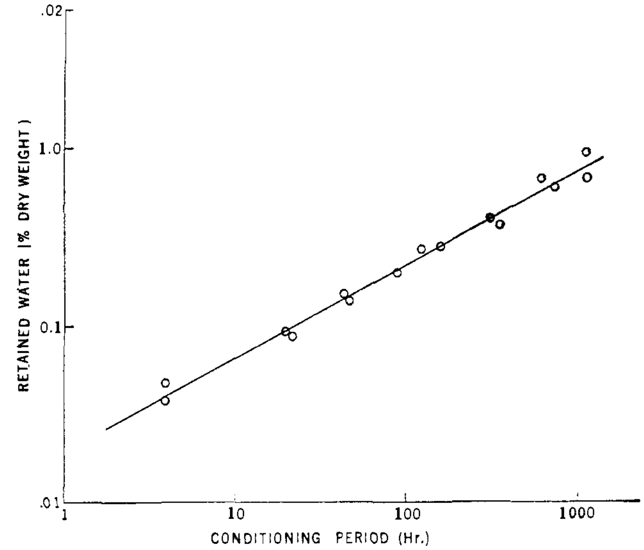

Figure 8. Retention of water on vacuum drying after conditioning samples for different periods.[80]

K. OTHER SORPTION STUDIES

These include the effects of pH on sorption and the sorption of sulfur dioxide, sulfuric acid, and copper on cellulose.

The absorption[82] of tetrakis(hydroxymethyl)phosphonium chloride by synthetic fibers at different pH levels showed that as the pH was increased from 2 to 8 the amount of sorbed material also increased markedly. Similar studies on paper and textile materials show the same results.[83,84] Typical results of the effect of pH on paper sorption are given in Figure 9. A

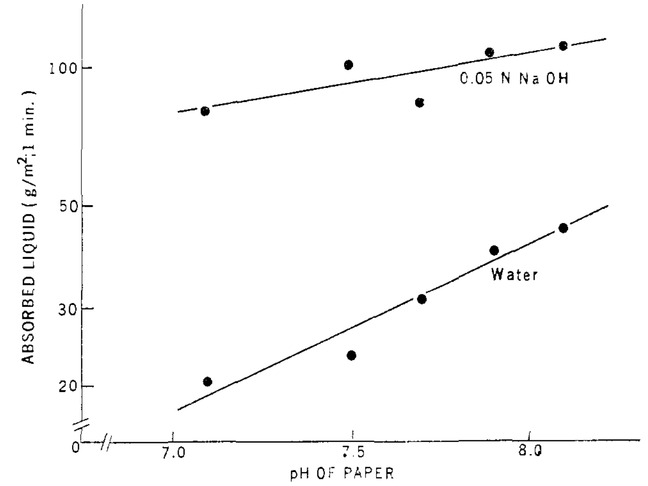

Figure 9. Effect of pH on sorption.[83]

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(80) G. N. Christensen and H. F. A. Hergt, *J. Polym. Sci., Part A-1*, 7, 2427 (1969).
(81) A. Venkateswaran, submitted for publication.
(82) R. S. Gandhi, *Text. Res. J.*, 38, 1180 (1968).
(83) J. A. Bristow, *Pap. Puu*, No. 11, 639 (1968).
(84) J. H. Bradbury, *J. Appl. Polym. Sci.*, 7, 533 (1963).

study[85] of the sorption of sulfur dioxide by cellulose showed that the sulfur dioxide sorbed was gradually converted to sulfuric acid, and its presence adversely affected the life of the material. Brodnyan[86] found that titanium dioxide has a greater affinity to sorb on a cellulose surface than an organic substrate like poly(*n*-butyl methacrylate). Experimental evidence[87] shows that the absorption of copper from solution by cellulose is due entirely to acidic groups in or associated with the cellulose molecules and that these sorption data give little information on the physical structure of cellulose. In another study, Bland[88] found that milled wood lignin sorbed more copper than cellulose, and he concluded that not only carboxyl groups are involved but also noncellulosic constituents of wood in the sorption of copper.

A sorption study[89] of Cu^{2+} and Co^{2+} ions on cellulose ion exchangers from different solvents showed that methyl alcohol, ethyl alcohol, or acetone are suitable media for ion exchange. The percentage and the rate of sorption were reduced when the permittivity of the solvent was decreased.

The effect of heating[90] on the absorption properties of unbleached sulfite pulp was investigated. The pulp was beaten to 25 and 65° Schopper–Riegler freeness. The absorption of Al^{3+} (from $Al(OH)_3$ solution) by the beaten and dried samples was lower than those of unbeaten samples and higher for the nondried pulp by a factor of nearly 2.5.

VII. Relation between Sorption and Other Properties of Wood and Cellulose

Sorption measurement is essentially a nondestructive test which, although very slow, has been used or correlated with many other properties of wood and cellulose.

A. ESTIMATION OF DIFFUSIVITY AND SOLUBILITY

The quantities are usually determined independently by the use of a combination of permeability and sorption measurements. According to Crank[91] it should be theoretically possible to measure both these quantities from a single sorption experiment and, in fact, it has been realized in practice.[92] For the analysis and interpretation of the sorption processes, Fourier's radial differential equation[92] was employed exclusively. The data satisfactorily fitted the equation in spite of the fact that there are numerous assumptions involved in the derivation. Careful measurements and analysis are necessary to reveal the systematic deviations of the fitted diffusion equations from the experiment. From these deviations some information could be gathered from simple sorption experiments into the behavior of the diffusion coefficient with respect to concentration and pressure. This method of calculation was applied to polyethylene.[92]

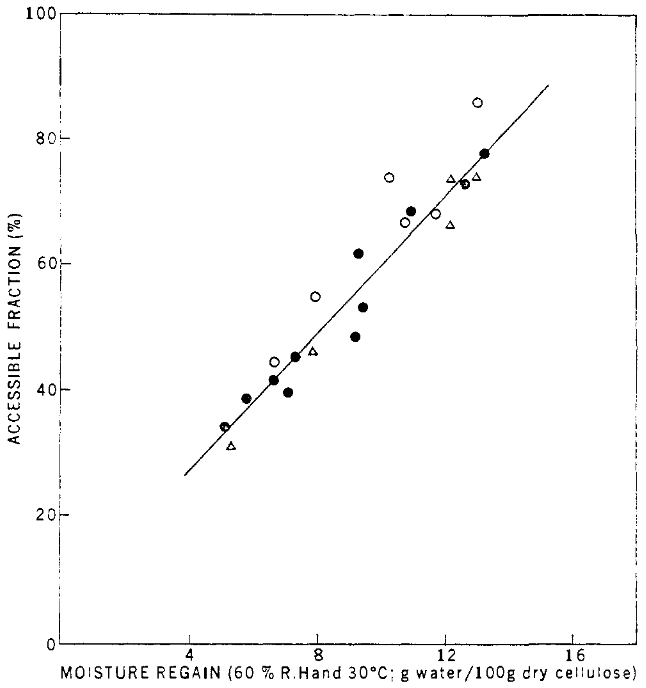

Figure 10. Relation between moisture regain and accessible fraction of various cellulosic materials.[96]

B. ESTIMATION OF ACCESSIBLE (NONCRYSTALLINE) REGION IN WOOD AND CELLULOSE

According to Hermans,[41] sorptive power is a function of the accessible portion (noncrystalline content) in cellulose, and hence a measure of sorption may be considered as a relative amount of the accessible region.

Following this concept, determinations[93–96] of accessible portion in wood and cellulose have been made using several sorbates. These include water vapor,[35] deuterium oxide vapor,[94,95] and tritiated water.[96]

The extent of $OH \rightleftharpoons OD$ exchange reaction between deuterium oxide vapor and cellulose (in the case of tritium exchange the reaction is $ROH + HTO \rightleftharpoons ROT + H_2O$) is usually determined by measuring the increase in the dry weight of the sample. The exchange takes place in two stages, first fast and then slow. The fractional accessible portion in many natural and regenerated cellulosic materials estimated by the deuterium exchange technique was found to be linearly related to the moisture sorption of the samples. The typical results are given in Figure 10. The scatter of results in Figure 10 is considerable, but there is little doubt that an approximately linear relationship exists between the two quantities. This relation is consistent with the generally accepted model for cellulose that it is a two-component system.[97]

Accessibilities of a variety of wood preparations were reported by measuring the extent of the exchange reaction between OH groups and water, using tritium as a tracer.[96]

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(85) C. J. Edwards, F. L. Hudson, and J. A. Hockey, *J. Appl. Chem.*, 18, 146 (1968).

(86) J. G. Brodnyan, *J. Paint Technol.*, 40, 139 (1968).

(87) R. I. C. Michie, *Nature*, 190, No. 4778, 803 (1961).

(88) D. E. Bland, *ibid.*, 190, No. 4778, 804 (1961).

(89) A. Lasztity, Zs. Remport-Horvath, I. Pozsonyi, and K. Veress, *Acta Chim.* (*Budapest*), 60, 41 (1969).

(90) L. G. Vinogradova and V. I. Yur'ev, *Mater. Nauch.-Tekh. Konf. Khim. Tekhnol. Fak., Leningrad. Lesotekh. Akad.*, 69 (1967); *Chem. Abstr.*, 71, 114359v (1969).

(91) J. Crank, "The Mathematics of Diffusion," Oxford University Press, Oxford, 1956.

(92) J. L. Lundberg, M. B. Wilk, and M. J. Huyett, *J. Polym. Sci.*, 57, 275 (1962).

(93) G. L. Dolgin and L. E. Akim, *Tr. Leningrad. Tekhnol. Inst. Tsellyul.-Bum. Prom.*, No. 21, 60 (1968).

(94) J. Dechant, *Faserforsch. Textiltech*, 19, 365 (1968).

(95) R. Jeffries, *J. Appl. Polym. Sci.*, 8, 1213 (1964).

(96) Y. Sumi, R. D. Hale, J. A. Meyer, B. Leopold, and B. G. Ranby, *Tappi*, 47, 621 (1964).

(97) A. Venkateswaran, *J. Appl. Polym. Sci.*, 13, 2469 (1969).

Birch wood had a lower accessibility (53%) than spruce (60%), and this difference was attributed to either the variation in the carbohydrate fraction or hemicellulose and lignin content in these woods. In both species 40% of the hydroxyl groups in lignin was found to be accessible to water, and the xylan portion in wood is relatively inaccessible.

C. RELATION BETWEEN SORPTION AND ELECTRICAL PROPERTIES OF CELLULOSE

Since the sorptive power of a fibrous material is directly related to its accessible portion, and since the accessible portion (which possess the freedom of movement) is largely responsible for electrical polarization, it has been suggested that permittivity should be directly related to the accessible part in cellulose.[98] Several studies[34,35,98,99] of water-vapor sorption by cellulosic materials proved this to be true. Typical results are given in Figure 11. The estimates of noncrystalline content in cellulosic materials by sorption technique agree well with those obtained from permittivity measurements.[97]

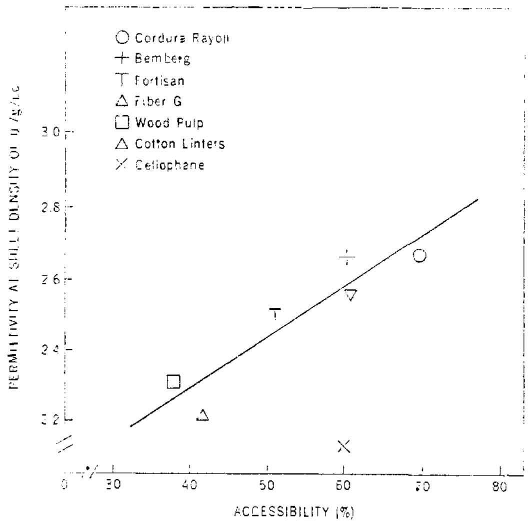

Figure 11a. Relation between accessibility and permittivity of cellulose.[34]

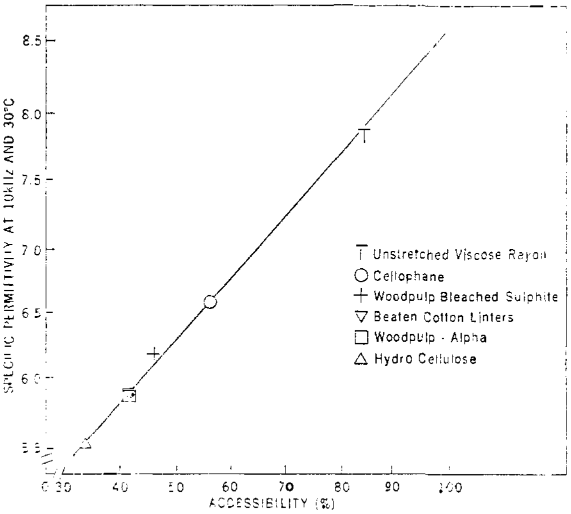

Figure 11b. Relation between accessibility and specific permittivity of cellulose.[35]

D. SORPTION AS A TECHNIQUE FOR STUDYING DETERIORATION OF WOOD

The ability for sorption of pine and spruce before and after attack by brown-rotting fungi was studied.[100] The hysteresis effect between sorption and desorption makes it possible to specify wood genera and subgenera and to measure fungi according to their intensity of deterioration reached in the same period of incubation.

E. RELATION BETWEEN SORPTION AND THERMODYNAMIC PROPERTIES OF WOOD

The thermodynamics of sorption includes various quantities such as swelling pressure, sorption isotherm, energy exchanges involved in sorption, and the specific heat of wood.

The sorption and desorption isotherms characterize the behavior of wood and cellulose exposed to various conditions of relative humidity. Strong swelling occurs at high values of relative vapor pressure. These isotherms are affected by temperature and previous history of the sample under test. According to Barkas,[51] mechanical restraint should affect the sorption isotherm of wood, cellulose, and other hygroscopic materials such as gels analogous to the effect of an external stress on the vapor pressure of an osmotic solution. The equation of the osmotic pressure may be written in the form[101]

$$h_1/h_2 = \exp(PV/RT) \qquad (6)$$

where h_1 and h_2 are vapor pressures of the gel before and after application of the stress P, V is the apparent specific molar volume of water in gel, R is the gas constant, and T the temperature (°K). Application of the above equation yielded a swelling pressure about twice the maximum value of the observed one.[101] This could be due to the fact that all voids in wood or cellulose were not compressed. Another factor is the compressibility of the cell wall itself, and this was not taken into consideration by Barkas in his equation.[51,52]

The heat of sorption can be determined either by the isosteric method or by the calorimetric method. To calculate the heat of sorption by the isosteric method, the variation of the vapor pressure of the sample with temperature at constant moisture content is determined. In the calorimetric method the heat of wetting at various moisture contents is measured. The heat of sorption (Q) and heat of wetting (W) are related by[101]

$$Q = -100\frac{\mathrm{d}W}{\mathrm{d}m} \qquad (7)$$

$$W = 0.01\int_m^F Q\,\mathrm{d}m \qquad (8)$$

where F is the percentage of moisture content of the saturated wood and m is the moisture content.

Regardless of the method used, the heat of sorption is interpreted as the binding energy between wood (or cellulose) and water, while the heat of wetting represents the available sorption sites for the accessibility of water.

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(98) C. R. Calkins, *Tappi*, **33**, 278 (1950).

(99) J. E. Algie, *Text. Res. J.*, **36**, 317 (1966).

(100) G. S. Dewitz, K. Lenhart, and F. Peschka, *Holztechnik.*, **10**, 113 (1969).

(101) C. Skaar and W. Simpson, *Forest Prod. J.*, **18**, 49 (1968).

(102) K. E. Kelsey, Division of Forest Product Technology, Paper No. 28, CSIRO, Australia, 1963.

According to Kelsey,[102] the specific heat of wood is related to thermodynamic changes associated with sorption of water. A satisfactory relation between specific heat of wet wood C_m, that of dry wood C_0, and moisture content m is given by[102]

$$C_m = \frac{C_0 + 0.01m + d[(w - \bar{w})/dT]}{1 + 0.01m} \qquad (9)$$

where $[d(w - \bar{w})/dT]$ is the change in the integral heat of sorption with temperature. Experimental data[101] on klinki pine show that this equation is adequate in explaining the observed results.

F. RELATION BETWEEN SORPTION AND TORSIONAL RIGIDITY OF CELLULOSIC MATERIALS

Following Peirce's findings[25] that the logarithm of relative rigidity of cotton is proportional to the moisture regain, Meredith[25] measured the relative rigidity of natural and regenerated fibers. The data obtained at 65% relative humidity fitted well into eq 10,[25] where M is the moisture regain corre-

$$\ln\left(\frac{G}{G_{65}}\right) = -0.82\left(\frac{M}{M_{65}} - 1\right) \qquad (10)$$

sponding to a rigidity modulus G, and M is the regain at 65% relative humidity. Typical results are shown in Figure 12. The water molecules associated with molecular segments of fibers were found to be linearly related to relative rigidity G/G_0 up to 90% relative humidity. The equation is[25]

$$\frac{G}{G_0} = 1 - \left(1 - \frac{\gamma^1}{\gamma}\right)\left(1 - \frac{G_c}{G_0}\right)\frac{C_a}{nA} \qquad (11)$$

where γ^1, γ, n, and A are constants, and C_a is the volume of water associated with molecular segments containing a number of molecules. The observed fall in rigidity was attributed to the breaking of hydrogen bonds between chain molecules in the noncrystalline region and that at saturation regain; one molecule of water is bound to each accessible polar group which would otherwise be linked to a similar polar group in a neighboring chain molecule by means of a hydrogen bond.

G. EFFECT OF SORPTION ON THE FLEXURAL CREEP BEHAVIOR OF WET AND DRY PROCESS HARDBOARDS

The elastic behavior of wood and cellulose is attributed to the stretching or straining of molecular bonds (covalent and secondary linkages of the crystalline and noncrystalline regions) and the uncoiling of molecular chain segments. The strain in crystalline portions is likely to be small, and since the noncrystalline fraction is not well oriented, it is possible that this fraction in the direction of an applied stress could undergo some chain straightening before bond stretching could occur.

Creep is believed to occur when bonds between neighboring molecules are broken and re-formed at different positions.[4] Removal of the load causes some of the new bonds to rebreak, resulting in partial recovery. There will be no recovery if the molecules at their stress-induced positions are satisfied to that extent that they cannot be restored to the original positions.

Experimental results show[4] that in wet and dry process hardboards sorption and desorption greatly increase creep formation. Creep during sorption from 5 to 10% m.c. is from two to three times greater than that occurring during desorption for the same moisture content range and that occurring at a 10% constant moisture. The magnitude of the creep was increased when the temperature and stress levels were increased combined or separately. Development of locked-in deformation was accelerated by sorption and desorption under load. The accelerated creep development during sorption or desorption is believed to be due to the increased rate of moisture movement and bond breakage created by nonequilibrium conditions.

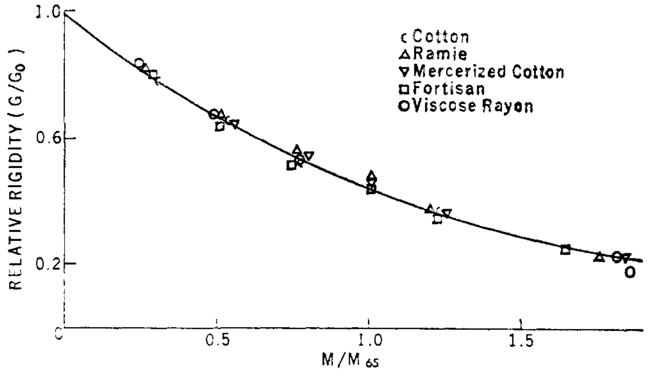

Figure 12a. Relation between moisture and relative rigidity of cellulosic materials.[25]

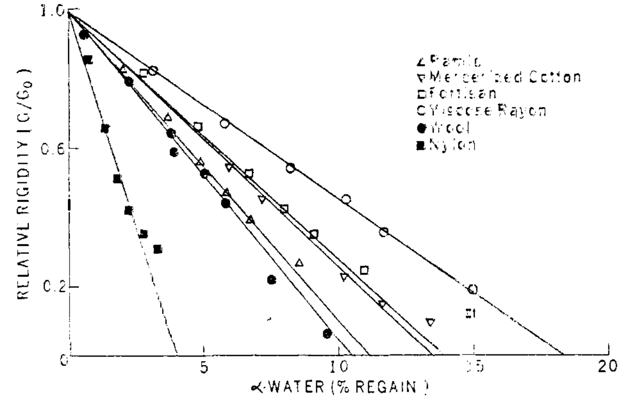

Figure 12b. Relation between regain and relative rigidity of cellulosic materials.[25]

VIII. Models Used for Interpretation of Sorption Isotherms

Many theoretical models have been postulated in an attempt to explain the sorption phenomena observed in polymers including wood and cellulose. Any model can be said to be satisfactory if it explains the observed phenomena, *viz.* the magnitude and shape of the sorption isotherm for the entire range of relative humidity, difference between sorption and desorption (hysteresis), swelling, heat effects following sorption, and correct temperature and tension dependence of isotherms. At present it seems there is no theory which will adequately explain all these phenomena.

Various models have been postulated, leading to as many as 20 sorption isotherm equations. These equations were derived on the basis of either kinetics and thermodynamics, statistical considerations, polarization mechanism, or mass and volume. Most of the equations are given in Table III in a

Table III

Isotherm Equations Reported in the Literature

Equation	*Symbols and remarks*	*Ref*	*Eq no.*
$\log V = \log k + \frac{1}{n}\log P$	V = volume of vapor sorbed P = pressure in cm k, n = constants depending upon media and temperature *Semiempirical parabolic equation*	103	12
$\frac{P}{V} = \frac{1}{kV_m} + \frac{P}{V_m}$	P = pressure in cm V = volume of vapor sorbed V_m = volume of vapor for the formation of a monolayer k = constant that depends on temperature *Theoretically sound hyperbolic equation*	105	13
$\left(1 - \frac{p}{P}\right) = (1 - kC_a)\exp(-\beta C_b)$	p/P = the relative vapor pressure in equilibrium with fibers C_a = the concentration of moisture in the "a" phase C_b = the concentration of moisture in the "b" phase k = a constant expressing the effect on the equilibrium of the evaporation of "a" molecules β = a constant which is an inverse measure of the dispersion of the cellulose *Two-phase theory*	120	14
$\ln\left(\frac{P_a}{k_3P_0}\right) = k_2k_1^a$	a = amount of material sorbed at pressure P_s k_1, k_2, k_3 = constants *Polarization theory*	120	15
$\log\left(\frac{P_s}{P}\right) = k_1k_3^a + k_4$	P_s/P = relative vapor pressure a = weight sorbed k_1, k_3, k_4 = constants *Polarization theory*	121	16
$V = \frac{V_mCX}{(1 - X)}\frac{[1 - (n + 1)X^n + nX^{n+1}]}{[1 + (C - 1)X - CX^{n+1}]}$	V = volume of sorbate X = relative vapor pressure V_m, C = constants at a fixed temperature n = numbers of layers *Derived kinetically*	109	17
$P = \frac{\theta}{(1 - \theta)}k\exp\left(\frac{2\theta w}{RT}\right)$	P = pressure of the gas θ = ratio of the quantity sorbed to maximum quantity sorbed k = constant $2w$ = interaction energy between one adsorbed molecule and z nearest neighbors where z is the coordination number R = gas constant T = absolute temperature in °K *Derived by statistical thermodynamics*	115	18
$\ln\left(\frac{P}{P_0}\right) = \ln V_1 + V_2 + \mu V_2^2$	P/P_0 = relative vapor pressure V_1, V_2 = volume fractions of water and polymer μ = semiempirical interaction parameter *Solution theory; thermodynamic approach*	114	19

Table III (Continued)

Equation	*Symbols and remarks*	*Ref*	*Eq no.*
$\frac{A}{B} = \frac{CX[1 - (n+1)X^n + nX^{n+1}]}{(1 - X)(1 - X + CX - CX^{n+1})}$	Same as BET *Statistical treatment*	116	20
$\frac{Mr}{1800} = \frac{kh}{1 - kh} + \frac{kk_1h}{1 + kk_1h}$	M = molecular weight of the operating polymer r = moisture regain h = relative humidity k, k_1 = "properly chosen" constants *Thermodynamic treatment; same idea as in Peirce's two-phase theory*	108	21
$(\alpha - X)(\beta - X) = \beta X^2$ $\ln\left(\alpha - \frac{X}{\alpha}\right) + \left(\frac{\mu N_1}{kT}\right) = \ln\left(\frac{P}{P_0}\right)$	β = localized sites in grams per gram of sorbent α = number of molecules sorbed X = number of molecules on localized sites at a given relative vapor pressure k = Boltzman's constant T = temperature in °K μN_1 = partial molar free energy of sorbate for the swelling of the sorbent from the dry state *Extension of Hill's treatment*	117	22
$\ln X = \ln V_1 + V_2 + \mu V_2^2 + \frac{KV_1'}{RT}\left(\frac{1}{V_2^{1/3}} - 1\right)\left(\frac{5}{3V_2^{1/3}} - 1\right)$	X = relative vapor pressure V_1, V_2, μ = same as eq 19 K = constant having the dimension of elastic modulus R = gas constant T = Kelvin temperature V_1' = partial molal volume of the sorbate *Extension of eq 19*	118	23
$C_a = nA\left[1 - \exp\left(-\frac{C}{nA}\right)\right]$	C_a = number of water molecules in "a" phase C = total number of water molecules n = number of hydrophilic groups per residue A = accessible fraction of the material *Modified Peirce's two-phase theory*	25	24
$\frac{V'}{V_s'} = 1 + n\left(\frac{V''}{V_s''} - 1\right)^{i/3}$	V' = specific volume of sorbate in the non-saturated state in the sorption space V_s' = specific volume of sorbate in saturated state n = number of layers V'' = specific volume of sorbate in the non-saturated state in the surrounding space V_s'' = specific volume of sorbate in the saturated space i = 0, 1, 2, 3 *Derived on the principle of deformation of space*	122	25
$\frac{X(1 - X^n)}{A(1 - X)} = \frac{1}{BC} + \frac{X(C - 1)}{BC}$	Same as in BET *General equation (BET is a crude special case of this)*	11	26
$U = a\phi^n + C_1 \exp[-{}^1/_2(b_1\Psi - 1)^2] + C_2 \exp[-{}^1/_2(b_2\Psi - 1)^2]$	U = total amount of sorption $a\phi^n$ = initial take-up $C_1 \exp(-{}^1/_2(b_1\Psi - 1)^2)$ = submicroscopic capillary condensation $C_2 \exp(-{}^1/_2(b_2\Psi - 1)^2)$ = microscopic capillary condensation $a, n, C_1, b_1, C_2,$ *and* b_2 = constants for each sorbent *Statistical treatment*	119	27
$\left(\frac{P}{P_0}\right) = \exp\left[\left(-\frac{18\beta\epsilon}{RT}\right)\exp(\beta r)\right]$	P/P_0 = relative vapor pressure r = moisture regain β, ϵ = constants R = gas constant T = temperature in °K *Derived thermodynamically*	113	28

Table III (Continued)

Equation	Symbols and remarks	Ref	Eq no.
$1 - \frac{v_a}{v_p} = \frac{\int_{r_a}^{\infty} (r - t)^2 f(r) \mathrm{d}r}{\int_0^{\infty} r^2 f(r) \mathrm{d}r}$ (sorption) $1 - \frac{v_d}{v_p} = \frac{q_b \int_{r_d}^{\infty} (r - t)^2 f(r) \mathrm{d}r}{\int_0^{\infty} r^2 f(r) \mathrm{d}r}$ (desorption)	v_p = volume of sorption at saturation v_a = volume sorbed during sorption v_d = volume sorbed during desorption r = radius of pore t = thickness of sorbate layer	111	29

chronological order. These equations developed in connection with the interpretation of sorption data have been applied to various polymer systems and not all have been tested for wood and/or cellulose in particular. These equations will now be discussed in some detail.

In 1909 Freundlich[103] proposed a semiempirical parabolic isotherm (eq 12) which was tested for the sorption of various gases on powders, charcoal, and fibrous materials. According to Brunauer,[104] this equation is applicable only to the middle pressure range. Later, Langmuir[105] put forward the first theoretically sound hyperbolic equation, eq 13, which has been widely applied. The influence of different electrolytes on the interaction of chlorazol sky blue FF with cotton fibers in aqueous solutions[106] and also the sorption of polyvinyl acetate on wood surface[58] are explained successfully by this simple equation.

Many of these equations (eq 14, 17, 19, 21, 24, 28, 29) were derived on the basis of kinetics and thermodynamics. Assuming that water is absorbed by fibrous materials in two phases (*viz.* the first phase in which water molecules are associated with molecular segments as a chemical compound, and the second phase in which water molecules fill the available spaces under attractive forces like those in a liquid), Peirce[107] proposed a two-phase model (eq 14) to explain sorption and elastic properties of cotton. This theory considers that fiber consists of crystalline and noncrystalline material and that the fractional noncrystalline portion represents the degree of accessibility of fiber to moisture. A modification of Peirce's equation (eq 24) explained[25] the relation between moisture sorption and relative rigidity satisfactorily for natural, regenerated, and synthetic fibers for a humidity range between 0 and 90%.

On the basis of the assumptions that the sorption of water vapor by polymers is governed by two sets of equilibria (the formation of a solution of water in the polymer and the formation of hydrates between water and definite units of molecular segments), Hailwood and Horrobin[108] derived an isotherm (eq 21) which has been widely applied for natural fibers[34,98,108] and wood.[19,30] In fact, this is the same idea as that used by Peirce in his two-phase theory, with the additional assumption that the mixture of polymer, polymer hydrates, and dissolved water forms a single solid phase. Note that their thermodynamical argument is more rigorous than that used by Peirce. In the application of this equation to any system, the choice of constants is an important factor for getting agreement with experiment.

A multilayer adsorption theory (eq 17), derived[109] kinetically assuming that condensation forces contribute principally to physical adsorption, has been applied to polymers with limited success.[110] This is essentially an extension of the Langmuir interpretation of monomolecular adsorption, with the added hypothesis that the formation of successive layers can occur by the adsorption of molecules on the top of a layer which has already been formed. As in the Langmuir theory, the rate of evaporation of the molecules in the first layer is considered to be equal to the rate of condensation on the uncovered surface. It is then similarly argued that the rate of evaporation of each succeeding layer is equal to the rate of condensation on the uncovered surface. The final equation is obtained by performing a summation. This equation has been successfully applied in the study of surface area of fibers.[22,23]

Considering the isothermal transfer at equilibrium of sorbate molecules from a bulk liquid phase, Nicholson[111] proposed (eq 29) a randomly arranged three-dimensional network of circular cylinders (pores) which might be expected to resemble an experimental system closer than the usually adopted parallel bundle model. This also could be developed as a model medium for one- and two-phase flow. Only distributions having a mean radius in the transition pore range 20–150 Å were considered. According to Chudina,[45] these pores mainly contribute to the formation of the internal surface in wood and play an important role in the adsorption process. This model has not been tested for either wood or cellulose.

Experimental results show that a simple relationship exists between moisture regain and heat of wetting of wood and fibrous materials. The relationship is[112]

$$q_i = q_0 \exp(-\alpha x) \tag{30}$$

where q_i is the integral heat of wetting of a fiber (cal/g of dry fiber) at moisture regain x, q_0 is the heat of wetting of dry fiber, and α is an adjustable constant. Using eq 30 as a basis, a two-parameter isotherm equation[113] (eq 28) was derived

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[103] H. Freundlich, "Kapillarchemie," Vol. I, Georg Thieme, Leipzig, 1930, p 153.

[104] S. Brunauer, "The Adsorption of Gases and Vapors," Vol. 1, Princeton University Press, Princeton, N. J., 1943, p 57.

[105] I. Langmuir, *J. Amer. Chem. Soc.*, 40, 1361 (1918).

[106] S. R. Sivaraja Iyer, G. Srinivasan, and N. T. Baddi, *Tex. Res. J.*, 38, 693 (1968).

[107] F. T. Peirce, *J. Tex. Inst.*, 20, T-133 (1929).

[108] A. H. Hailwood and S. Horrobin, *Trans. Faraday Soc.*, 42B, 84 (1946).

[109] S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, 60, 309 (1938).

[110] H. B. Bull, *ibid.*, 66, 1499 (1944).

[111] D. Nicholson, *Trans. Faraday Soc.*, 64, 3416 (1968).

[112] D. N. E. Cooper and D. K. Ashpole, *J. Text. Inst.*, 50, T-223 (1959).

[113] N. T. Anderson and J. L. McCarthy, *Ind. Eng. Chem., Process Des. Develop.*, 2, 103 (1963).

and correlated with data for 30 systems comprising wood, natural, regenerated, and synthetic fibers in equilibrium with water vapor. The isotherm equation was valid over the 10–85% relative humidity range.

A number of the isotherm equations are based on a statistical treatment[11,114–119] (eq 18, 20, 22, 23, 26, 27). These isotherms have been applied to either cellulose–water or wood–water system. The solution theory (eq 23) of Rowen and Simha[118] is essentially an extension of the Flory–Huggins theory[114] (eq 19), while the White–Eyring isotherm[117] (eq 22) is an extension of Hill's treatment[116] (eq 20). More recent statistical isotherms (eq 26 and 27) have been successfully applied to cellulose and wood for a wide range of relative humidity.

The formation of thick films was studied[120,121] by considering the free energies of adsorbed films. Isotherms (eq 15 and 16) for such films have been derived[120,121] for the assumed system of a strongly sorptive polar surface or group which adsorbs a first layer. Subsequent layers are sorbed because of the dipoles induced in the first layer, which polarize the second layer, and this in turn can attract a third layer and so on. Identical with these eq 15 and 16, which were derived from the polarization theory, Anderson and McCarthy[113] obtained a two-parameter isotherm (eq 28) from thermodynamic consideration. Because of the simplicity and generality, this equation should be useful for prediction, interpolation, and extrapolation of sorption data in fibers/wood–water systems.

A recently advanced theory,[122] based on the "principle of deformation of space," is a radical new approach to the physical problem of sorption and gives a general sorption equilibrium isotherm (eq 25). In the derivation no concept other than mass and space was used. This theory explains wood–moisture relationships, such as sorption, desorption, hysteresis, swelling, and shrinkage. The evaluated thermodynamic data from this equation also agree well with the experimental results.[32]

IX. Comparison of and Comments on the Various Models

The isotherm equations given in Table III are mathematical representations which resulted from various models that either confirm or refute the assumptions made in deriving them. In a sorption process certain assumptions are commonly made. These include the following: the energy of adsorption of the first amount of material sorbed is measurably different from that of the material subsequently adsorbed; the energy of adsorption of all but the first portion remains constant and equal to the energy of condensation of the sorbed material; there is no appreciable energy of interaction between adjacent molecules adsorbed on the surface. In deriving any isotherm one or more assumptions are involved. Although none of these isotherms describes the sorption process observed in polymers completely, it is interesting to review and compare wherever possible.

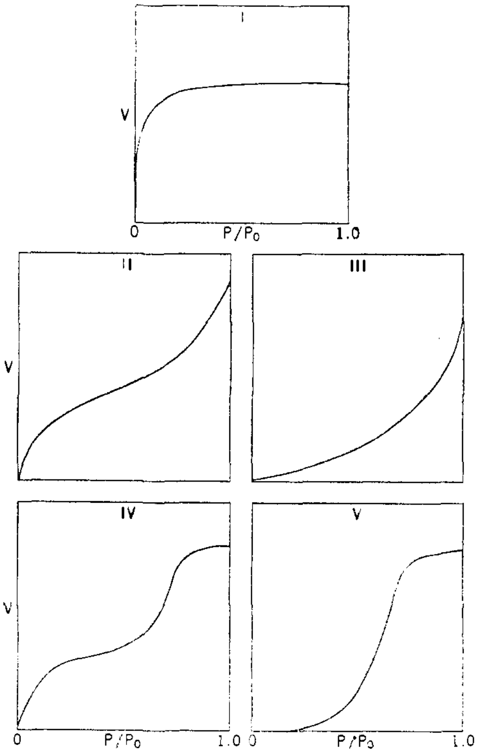

Figure 13. Various types of isotherms for physical adsorption.[109]

The Freundlich equation[103] was most successful in representing sorption data of synthetic fibers at very low vapor pressures. Many of the other equations were not tested for the very low vapor-pressure region. But, according to Taylor,[123] the theoretically valid Langmuir equation[105] is completely inapplicable to this region. He believes that variation in the heat of adsorption and the creation of new sorbent centers occurring as sorption progresses could explain this. The BET equation also is inapplicable since it is purely an extension of the Langmuir equation.

The usually observed isotherm for wood/cellulose–water system cannot be fitted by the Langmuir equation. The Langmuir equation fits only where monomolecular surface adsorption occurs.

The inapplicability of these models at low pressures are attributed[124] to the inhomogeneities of real surfaces, and, at higher relative vapor pressures, to the disturbance caused by capillary condensation or filling up of narrow capillaries. Calculations made with a radically oversimplified model[124] showed that the BET method, when applied with necessary care, yields reliable results for the surface areas over a relative vapor pressure range between 0.1 and 0.4. This reliability was confirmed by a direct comparison between the surface areas obtained by BET procedure and another independent method.[125]

The desorption isotherm of a type II BET model (Figure 13) is often used to obtain a pore size distribution function. This type of analysis needs two important assumptions: that the system is a bundle of independent capillaries and that ther-

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(114) R. Simha and J. W. Rowen, *J. Amer. Chem. Soc.*, 70, 1664 (1948).

(115) H. L. Doppert, *J. Polym. Sci., Part A-2*, 5, 263 (1967).

(116) T. L. Hill, *J. Chem. Phys.*, 14, 263 (1946).

(117) H. J. White and H. Eyring, *Text. Res. J.*, 17, 523 (1947).

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(120) J. H. de Boer and U. Zwicker, *Z. Phys. Chem.*, 133, 407 (1929).

(121) S. Bradley, *J. Chem. Soc.*, 1467 (1936).

(122) L. Malmquist, "Sorption as Deformation of Space," Kylteknisk Tidskrift, No. 4, Stockholm, Sweden, 1958, p 1.

(123) J. B. Taylor, *J. Text. Inst.*, 43, T-489 (1952).

(124) G. Schay, *Period. Polytech., Chem. Eng.*, 9, 187 (1965).

(125) G. Schay, *Magy. Kem. Lapja*, 173 (1964).

modynamic equilibrium occurs only in desorption since desorption represents a lower chemical potential than sorption. In the case of compacted materials is which gas-flow studies are made, the first assumption is not realistic, while the second one is open to question since calorimetric studies showed that sorption on porous materials was reversible and that surface areas calculated from sorption measurements agreed more closely with those calculated from desorption measurements.[111] Analysis from a randomly arranged three-dimensional network of circular cylinders shows that pore-size distributions can be found from sorption isotherm, and a method has been developed for the same.[111]

The equations obtained from statistical treatments show that the BET equation is only a special case of such treatment. Cassie[126] and Pickett[127] have respectively derived and modified the BET equation from statistical considerations. But, according to Hill,[116] Cassie's derivation[126] of the BET equation is based on an incorrect argument and Pickett's modification[127] lacks theoretical justification. Note that the BET model has the advantage that it presents no mathematical difficulties. Experimental results[11] show that a somewhat refined multimolecular adsorption theory is capable of predicting capillary condensation for suitable values of parameters. This suggests that the ideas of multimolecular adsorption and capillary condensation are not really in conflict as is generally assumed.[11]

Rounsley's multimolecular adsorption equation (derived using several more additional assumptions than those usually used), although applicable to the entire range of relative vapor pressures, suffers from the same fault as the BET equation—it tends to give high adsorption values at very low humidities. It is also shown that BET equation is a special case of this equation. The White–Eyring model[117] (essentially an extension of Hill's treatment)[116] seems to be complex and unwieldy and reflects the proposition that sorption occurs by a variety of overlapping steps. The application of this equation to various cellulosic materials shows surprisingly good agreement between theoretical and experimental sorption and desorption isotherms, considering the many approximations involved. The statistical treatment of Flory shows good agreement for polymer solutions in the high relative vapor pressure range. A comparative sorption study of cellulose–water system between Flory–Huggins theory and BET shows that BET gives very poor agreement beyond a relative vapor pressure of 0.5 (Figure 14).

The Hailwood and Horrobin approach, which has a better theoretical basis than Peirce's two-phase theory, has been widely used for wood–water, wood–ammonia, and cellulose–water systems.[30] Although it has been applied with considerable success to these systems, its application to other polymers (such as protein) has been questioned. Furthermore the basic assumptions involved in its derivation also have been criticized.[128,129] But the equation gives a reasonable agreement if the choice of constants in the equation is properly made. For example, in the case of cotton fibers the difference between the observed and calculated regains was about 15%[108] for one set of constants while in the case of a polyester fiber using another set of constants the difference was as high as 50%.[6] The agreement between the calculated and observed regains seems to depend to a large extent on the type of fiber.

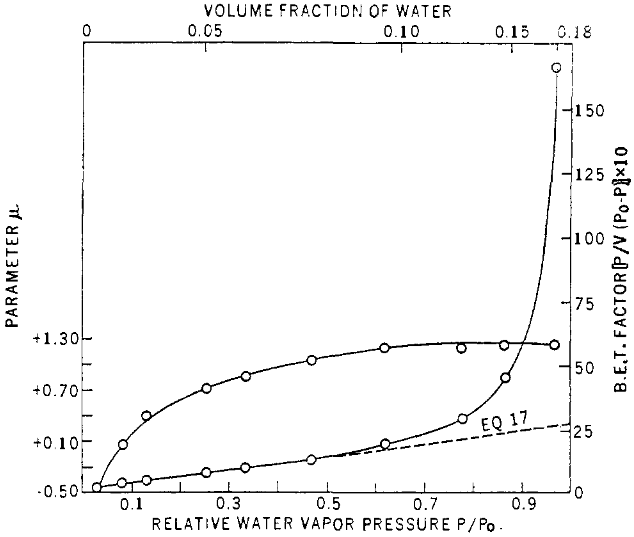

Figure 14. Comparison of eq 17 and 19 to cellulose–water system.[114]

Several workers[19,30,45] have calculated the so-called "monomolecular layer" thickness using both the Hailwood and Horrobin and BET models. With a structure like wood or cellulose the idea of a surface on which adsorption can take place is conceptually difficult. With plane surfaces adsorption is usually limited to the formation of a layer of one molecule deep. On the other hand, in wood or cellulose, there must be spaces of all possible sizes and shapes. The so-called monomolecular fraction of the total sorption calculated as per the Hailwood and Horrobin model is as high as 8.97% for unextracted wood–water system during desorption,[19] 6.47% during sorption,[19] and 16.5% for the wood–ammonia system.[30] The calculated value from the BET model for wood[45] was about 5% and for nylon less than 2%.[28]

The isotherm equations based on the polarization theory were applied to several polymer systems with considerable success.[113] Although the application of these equations to molecules with large permanent dipoles are justified, the derivation of such an equation and its application to sorption of gases with induced dipoles have been severely questioned.[109] It is interesting to note that an equation identical with these was derived from thermodynamics.[113] A comparison between this thermodynamically derived polarization equation, the White–Eyring, and the Rounsley models is given in Figure 15. Both the White–Eyring and the Rounsley equation are three-parameter equations derived specifically to include the effects of swelling at high relative vapor pressures. Figure 15 shows that eq 28 represents isotherm data in the high humidity region more successfully when compared with Rounsley's model. Equations 22 and 28 represent data equally well over a large range of relative humidity although eq 22 is more complex and the adjustable three parameters particularly in this equation are difficult to estimate by the method of least squares. Another advantage of eq 28 is that it can be used to describe the isotherm relationships without any prior knowledge of equilibrium conditions in a system knowing the magnitudes of β and $\beta\epsilon$.

There seems to be a good agreement between eq 25 and 27 for the wood–water system. Further, although eq 25, applied to a wood–water relationship, gives a very simple and unified explanation of the essential phenomena of sorption, desorp-

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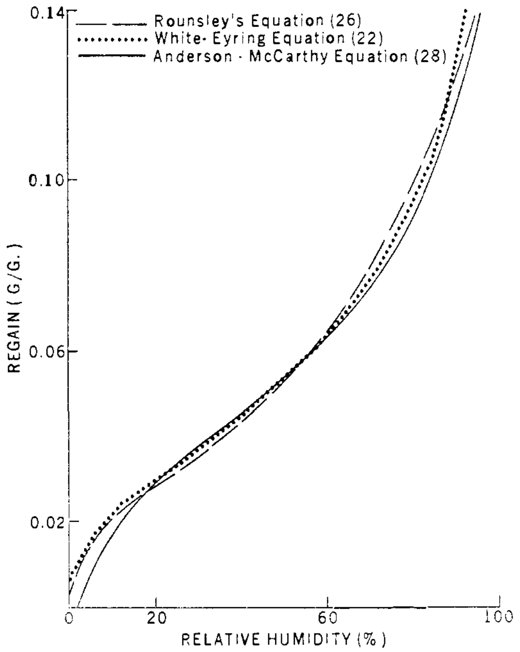

Figure 15. Comparison of eq 22, 26, and 28.[113]

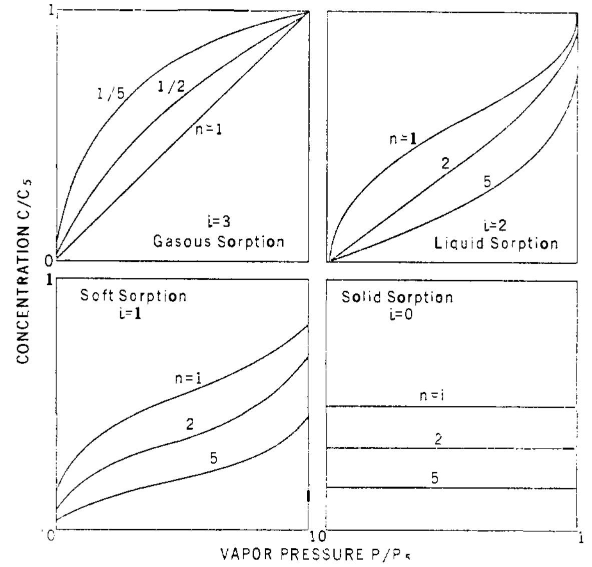

Figure 16. Ideal sorption isotherms according to Malmquist.[130]

tion, and swelling over the range of condition studied, additional work is needed to prove its applicability to the entire range of sorption and to other phenomenon such as adhesion and to give a complete physical picture of sorption. A comparison between the ideal sorption isotherms according to Malmquist[130] and the various sorption isotherms experimentally observed in physical adsorption are given in Figures 13 and 16 for comparison.

X. Conclusions

Sorption studies of wood and cellulose are very important since the presence of sorbed materials changes the physical, mechanical, chemical, and electrical characteristics of these materials. Past work has not given us a clear understanding of the basic principles of the sorption mechanism.

Although the characteristics of the sorption and desorption curves for a wide range of relative humidity are established, their nature at and in the immediate vicinity of 100% relative humidity are not clearly established. Whether the hysteresis loop is open or closed in this range is not known. Gathering sorption data in this range is certainly difficult experimentally since condensation occurs on samples as well as on the weighing system, unless extremely fine temperature control is maintained.

Since the conditioning period of samples influence significantly the percentage of water retained by the sample, it may not be possible to reproduce the same vacuum-dry weight after a subsequent conditioning (since the water molecules bound to cellulose molecular segments during conditioning may be inseparably bound to cellulose), and consequently the closure of the hysteresis loop at very low vapor pressure is also open to question.

The effect of temperature on shrinkage of dry and moist wood has not been clearly established. A detailed study of this phenomenon would be desirable since it influences significantly the behavior of wood dried at high temperatures and dried from a frozen condition.

The previous history of the sample is an important factor in the study of sorption. Most of the reported sorption studies on wood and cellulose fibers failed to recognize this.

The models proposed in the literature have not adequately explained the sorption mechanism on molecular level. Representation based on a pore size distribution mechanism would be most fruitful.

Although there are numerous equilibrium models suggested in the literature to explain sorption in polymers, all were not tested for wood and/or cellulose. Further, these theories differ in their underlying assumptions and in the approximations made in their derivations. Every formula seems to be satisfactory for one particular region of the total sorption range and to explain certain aspects of sorption process. Therefore, an agreement between any of these theories and experiments is not necessarily a sufficient test of the theory.

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