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THE INTERNAL SURFACE OF CELLULOSIC MATERIALS

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THE INTERNAL SURFACE OF CELLULOSIC MATERIALS¹

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Introduction

Cellulosic materials have two different types of internal surface: (a) the surface of the microscopically visible structure consisting of either tubular capillaries, such as the lumen of fibers in natural organized cellulosic materials, or the interfiber spaces of such processed cellulosic materials as paper, thread, or fabric; and (b) the surface of the transient capillaries within the cell walls of all types of cellulosic materials that exists only in the presence of a swelling agent.

The microscopically visible surface can be estimated from microscopical measurements, from sorption measurements of nonswelling gases or liquids, from the selective adsorption of a solute from a nonswelling solvent, or from the permeability of a mat of fibrous materials to liquids. The surface of the transient capillaries within the cell wall can be estimated from the sorption of polar vapors or liquids, from the selective adsorption of a solute from a swelling solvent, and from a combination of heat of swelling and adhesion tension data. The two different types of surface have been estimated by each of these various means from data taken from the literature and from new data on the selective adsorption from solution by different cellulosic materials.

Experimental Selective Adsorption Measurements

Thin cross sections of sugar pine about 1 mm. in the fiber direction and 5 mm. in the other directions were extracted in a Soxhlet apparatus for 4 days in alcohol, 7 days in an alcohol-benzene mixture, 2 more days in alcohol, and then 5 days in water. One to 3 grams of these sections or of analytical filter paper were weighed into a sample bulb, oven dried, and again weighed. About 20 cc. of solvent (either well-dried benzene, ethyl alcohol, acetone, or water) was added. The bulb was evacuated to remove the air from the cellulosic material and then weighed. A weighed amount of a standard solution of stearic acid in either of the 3 organic solvents or of

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phenol in water was added. The bulb was sealed with a glass stopper and held in a thermostatically controlled bath at 30° C. for 48 hr., which was shown to be sufficient for the attainment of equilibrium. The change in concentration of the equilibrium solution from the calculated original value was determined analytically. Blank determinations were also made in order to make slight acidity corrections.

The solutions of stearic acid were analyzed by evaporating the solvent on a steam bath and dissolving the stearic acid in 95 percent ethyl alcohol which had been made neutral to phenolphthalein. The stearic acid was then determined volumetrically with a microburet, using standard sodium hydroxide and phenolphthalein.

The concentration of phenol in aqueous solutions was determined by the potassium bromate-potassium iodide method. This method could not be applied to alcohol or benzene solutions of phenol because of the reactivity of the solvent.

The selective adsorption was calculated from the equation:

$$S = \frac{M\Delta C}{X(1-C)} \quad (1)$$

in which S is the selective adsorption of either solute or solvent in grams per gram of adsorbent, X is the weight of the adsorbent, M is the weight of the solution, C is the equilibrium concentration in grams of solute per gram of solution in the case of positive adsorption or of grams of solvent per gram of solution in the case of negative adsorption, and ΔC is the corresponding concentration change.

The calculated adsorption values are shown graphically in Figures 1, 2, and 3. It is of interest that stearic acid is positively adsorbed from a benzene solution, whereas the solvent is selectively adsorbed from solutions of stearic acid in alcohol and in acetone.

The tangential swelling of dry sugar pine was determined at the maximum concentration in which the different solutions were used. The values relative to unit swelling in water are as follows: stearic acid and phenol in benzene, 0.0; stearic acid in acetone, 0.56; stearic acid in ethyl alcohol, 0.84; phenol in water, 1.48. The data indicate that even a polar solute, such as phenol, when dissolved in nonpolar benzene, is not able to enter the cell-wall structure. Phenol-water solutions however, are able to enter the cell-wall structure to a greater extent than water alone.

Internal Surface of the Microscopically Visible Capillary Structure

The microscopically visible internal surface of soft woods (coniferous or needle-leaved woods) can be readily estimated from the average diameter of the lumens of the fibers and the number of lumens in a square centimeter

of cross section, by assuming that the lumens are continuous cylindrical tubes and neglecting the relatively small proportion of resin ducts and ray cells. In this way the internal surface of sugar pine with a dry volume specific gravity of 0.34 was estimated to be 2.5×10^3 cm.² per gram. Wood with a higher specific gravity will have a correspondingly lower microscopically visible internal surface.

The external surface of pulps or low-density paper can be roughly estimated from the dimensions of an average fiber, assuming that a relatively small fraction of the surface is utilized in fiber-fiber bonding. Howell and Jackson (11) have estimated in this way that paper made from pure cotton cellulose has a surface of approximately 1.6×10^3 cm.² per gram.

Kozeny (12) has developed a theoretical relationship between the internal surface of a filter-bed material and the permeability of the bed to liquids. Carman (6, 7) has shown that this relationship holds for granular material, while Wiggins, Campbell, and Maass (20) have shown that it applies to a mat of rods. They determined the permeability of a mat of cellulose acetate yarn fibers to benzene and from this they calculated the effective fiber surface to be $3.0 \pm 0.5 \times 10^3$ cm.² per cm.³ of actual material comprising the bed, or about 2×10^3 cm.² per gram.

Emmett and DeWitt² determined the absorption of nitrogen on electrical insulating paper at -195° C. This temperature is appreciably below the critical temperature for nitrogen, so that capillary condensation as well as true surface adsorption occurred. Hence, it was necessary to determine the part of the adsorption which is true surface adsorption in order to calculate the extent of the surface. Emmett and Brunauer (8) had previously made similar measurements on various catalytic materials and calculated the surface areas on the basis of different definable points on the adsorption curve representing the transition between true surface adsorption and capillary condensation. From this study they concluded that the inflection point of the sigmoid adsorption curve, which they called the B point, gives the best approximation for the limit of true surface adsorption. Sheppard and Newsome (13) and Stamm (15) had also come to the same conclusion for cellulosic materials. Two different insulating papers gave inflection points at a vapor pressure of about 10 cm. of mercury and at 0.125 and 0.127 cc. of nitrogen adsorbed per gram of paper, from which they calculated a surface value of 5.5×10^3 cm.² per gram.

The microscopically visible internal surface, S , per unit weight of cellulosic material was estimated by the authors from the selective adsorption data for stearic acid adsorbed from benzene, given in Figure 1, and the relationship

$$S = \frac{S_m \times N \times W}{M} \quad (2)$$

in which S_m is the cross section of the absorbed molecules, N is Avogadro's number (6.06×10^{23}), W is the molecular weight of the adsorbate per unit weight of adsorbent, and M is the molecular weight of the adsorbate. The

²Unpublished data kindly furnished by the authors.

maximum adsorption values, \bar{W} , and the cross section of the stearic acid molecule, \bar{S}_m (1), obtained from spreading measurements (21.0×10^{-16} cm.²) were substituted in the equation, giving a surface of 2.2×10^3 cm.² per gram for the sugar pine (dry volume specific gravity of 0.34) and a surface of 2.7×10^3 cm.³ per gram for the filter paper.

A summary of all the different microscopically visible surface values obtained by different methods is given in Table 1. All the methods give values of the same order of magnitude. It is of interest that the internal surface of the tubular structure of wood is of the same order of magnitude as the internal surface of sheets and mats of cellulose in which the surface is largely an interfiber surface.

Table 1.--Internal surface of microscopically visible capillary surface of different cellulosic materials

Material	Method	Internal surface
		cm. ² per gram $\times 10^{-3}$
Sugar pine.....	Microscopic measurement.	2.5
Sugar pine.....	Adsorption of stearic acid : from benzene.	2.2
Paper (cotton).....	Microscopic measurement.	1.6
Paper (electrical insulating)	Adsorption of nitrogen.	5.5
Paper (filter).....	Adsorption of stearic acid : from benzene.	2.7
Cellulose acetate yarn.....	Permeability to benzene....	2.0

Internal Surface of the Swollen Cell-Wall Structure

Grace and Maass (9) have determined the sorption of dry carbon dioxide, sulfur dioxide, ammonia, and hydrogen chloride by dry cotton and by dry white spruce. The sorption by cotton on a percentage weight basis for practically saturated vapors at 22° C. was 5.0 percent for sulfur dioxide, 4.0 percent for ammonia, and 2.0 percent for hydrogen chloride. The sorption by the white spruce on the same basis was 1.0 percent for carbon dioxide, 13.6 percent for sulfur dioxide, 7.4 percent for ammonia, and 10.5 percent for hydrogen chloride.

The internal surfaces of the swollen cell-wall structure of cotton and white spruce were calculated from the foregoing data, using equation 2. The values are given in Table 2, together with those for other systems. Except in the case of carbon dioxide, the values obtained with the different gases are in good agreement. The low value for carbon dioxide is not

surprising, as this gas would not be expected to have an appreciable swelling effect upon cellulosic materials.

Table 2.--Internal surface of the swollen cell-wall structure of wood and cellulose

Material	Method	Internal surface
		cm. ² per gram x 10 ⁻⁶
	(:Adsorption of CO ₂	0.4
White spruce.....	(:Adsorption of SO ₂	3.5
	(:Adsorption of NH ₃	4.3
	(:Adsorption of HCl	3.7
Sitka spruce.....	Adsorption of H ₂ O	3.5
Spruce (groundwood)..	Adsorption of CH ₃ OH	4.1
	(:Adsorption of H ₂ O from NaCl solution	4.0
	(:Adsorption of H ₂ O from glycerol solution	4.0
Sugar pine.....	(:Adsorption of phenol from H ₂ O solution	4.2
	(:Adsorption of C ₂ H ₅ OH from stearic acid solution	3.4
	(:Adsorption of (CH ₃) ₂ CO from stearic acid solution	3.0
White spruce.....	Heat of swelling and adhesion tension of H ₂ O	2.4
	(:Adsorption of SO ₂	1.3
	(:Adsorption of NH ₃	2.3
Cotton.....	(:Adsorption of HCl	0.9
	(:Adsorption of H ₂ O	2.2
	(:Heat of swelling and adhesion tension of H ₂ O	1.4
	(:Adsorption of H ₂ O	2.7
Sulfite pulp.....	(:Adsorption of CH ₃ OH	2.7
	(:Heat of swelling and adhesion tension of H ₂ O	1.8

The sorption measurements from which these calculations were made were conducted at a temperature which in all cases was below the critical temperatures of the gases. There is thus the possibility of some capillary condensation having occurred within the cell walls. This would tend to make the calculated internal surfaces somewhat high. The fact that these values agree very well with the values obtained from the following systems in which

capillary condensation has been duly accounted for indicates that capillary condensation must be small for these gases under the experimental conditions.

Capillary condensation accounts for a large part of the sorption of water vapor by cellulosic materials. The inflection point in the sigmoid moisture content-relative vapor pressure curves has been considered as representing the limit of surface adsorption. This seems justifiable on the basis of the measurements of Emmett and Brunauer (8) previously cited and on the basis of the theoretical considerations given by Sheppard and Newsome (13). They picture the sigmoid adsorption curves as being made up of a true parabolic surface adsorption curve that is concave to the relative vapor pressure axis and of a capillary condensation curve that starts at the relative vapor pressure corresponding to molecular-sized capillaries and exhibits the reverse curvature to that of the true surface sorption curve. This contention is further confirmed by the fact that the inflection point occurs at a relative vapor pressure corresponding closely to that which would exist over a capillary with a diameter about twice that of the water molecule. All the water held in such a capillary would be adsorbed on the surface.

There is a definite hysteresis effect in the sorption of water vapor and alcohol vapor by cellulosic materials. The desorption values are in all cases greater than the corresponding adsorption values over the whole relative vapor pressure range (15, 18, 19). Different results would thus be obtained for the calculated internal surface under these two conditions. In the case of the sorption of water vapor by Sitka spruce, the inflection point (18) on an oscillating relative vapor pressure-desorption curve (7.0 percent moisture content), which is intermediate between the corresponding values on true desorption and adsorption curves, was used in the calculations. In the case of the sorption of water and methyl alcohol vapors by sulfite pulp and cotton, the average sorption at the inflection point for desorption and adsorption conditions was used. The surface sorption value used for water adsorbed by cotton was 4.5 percent (19) and by sulfite pulp, 5.5 percent (5). The surface sorption value used for the adsorption of methyl alcohol by spruce groundwood was 10.0 percent (5) and by sulfite pulp, 6.5 percent (5). The internal surface was calculated from these data, using equation 2. In the case of water vapor, the molecular cross section was estimated from the density of liquid water at the freezing point by assuming the molecules to be spherical, as in the case of the various gases. The cross section of the alcohol molecule was taken as 21.6×10^{-16} cm.², the value obtained from film studies (1). The values for the internal surface of the swollen cell walls of the different cellulosic materials calculated from these data for the surface sorption of both water and methyl alcohol vapor are given in Table 2. These values are in good agreement with the values obtained from adsorption data for different gases which cause swelling.

The internal surface of the water-swollen cell-wall structure of cellulosic materials can also be estimated from the selective adsorption from solution. Stamm and Hansen (17) determined the selective adsorption of water from aqueous solutions of sodium chloride and of glycerol by sugar pine. As

the concentration of these solutions is increased, a limiting low selective adsorption of water which no longer acts as a solvent is approached. This was about 4.0 percent of water in both cases. Water that is selectively adsorbed from solution on the surface of the cellulosic material is not prevented from acting as a solvent for the dissolved solute. The surface-held water may share its bonds between the cellulose surface to which it is adsorbed and solute molecules in the vicinity of the selectively adsorbed water. If the bonds are arbitrarily considered to be equally shared, then the surface-adsorbed water is twice that which does not act as a solvent. On this basis the selective adsorption of water is 8.0 percent. This corresponds to an internal surface of the swollen cell-wall structure of approximately $4.0 \times 10^6 \text{ cm.}^2$ per gram of wood.

Similar calculations were made from the data of Figure 2 on the basis of the alcohol and the acetone bonds being equally shared between the wood and the stearic acid. Limiting selective adsorption values of 12 and 14 percent are thus obtained for the alcohol and the acetone, respectively. The internal surfaces calculated from those values, using 21.6×10^{-16} and $20.5 \times 10^{-16} \text{ cm.}^2$ for the cross-sectional area of the ethyl alcohol and acetone molecules (1), are also in good agreement with the previously calculated values (Table 2).

The internal surface of the swollen cell walls of wood was estimated from the selective adsorption of phenol from aqueous solutions (Figure 3). Because of the limited solubility of phenol in water at 30° C. maximum adsorption was not obtained, but it appears to approach a value of 27 percent. The internal surface calculated from this value and a molecular cross section of $24.0 \times 10^{-16} \text{ cm.}^2$ (1) is slightly higher than the other values. This may be due to the fact that phenol-water solutions cause a greater swelling than water alone, and may, as a result, create new sorptive surfaces. There is also the possibility of a slight solvent action upon the lignin of the wood, which would affect the results to some extent.

In a previous publication one of the authors (14) estimated the internal surface of the cell-wall structure of wood from adsorption compression data to be $0.3 \times 10^6 \text{ cm.}^2$ per gram. More recent adsorption compression data (16) give a larger calculated surface of the general order of the other values given in Table 2. The method, however, involves the questionable assumption that the different surface layers cover the same area. For this reason little significance is placed on the approximate agreement.

Bartell and Fu (4) have developed a relationship for calculating the internal surface of an adsorbent material, α , from the heat of adsorption or swelling, $-H$, and the adhesion tension, A , between the solid and the liquid, thus:

$$\alpha = \frac{-H}{A - \frac{A}{\delta} T \frac{d\delta}{dT}} \quad (3)$$

in which δ is the surface tension of the liquid and T is the absolute temperature. Values for the internal surface of cellulosic materials have been