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Swelling of Wood

Part II. Swelling in Organic Liquids

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Summary

The rate and maximum swelling of several North American wood species in 40 organic liquids have been obtained with a computer interfaced linear variable displacement transformer. Since wood swells very fast in some organic liquids, even at room temperature, this apparatus made it possible to obtain accurate rate data on the swelling of wood in organic liquids. It was found that many similarities existed between wood and cellulose maximum swelling within various solvent chemical classes. Hence, it appears that cellulose is the primary wood polymer responsible for the major amount of swelling of wood. In general, all the liquids, with a molar volume greater than 100 cc or with a small hydrogen bonding parameter, caused very little equilibrium swelling. The logarithm of the rate of wood swelling (In k) in the liquids was inversely correlated with the solvent molecular weight as well as with the molar volume of the solvent, that is, the larger the solvent molecular size, the slower the rate of swelling. The Ink also was strongly correlated with the maximum tangential swelling of wood. The maximum tangential swelling for all wood species was linearly correlated with the solvent basicity (donor number). Other solvent properties such as volubility parameter, dipole moment, dielectric constant, and surface tension showed very weak correlations with the maximum tangential swelling of wood in organic liquids.

Introduction

The phenomenon of swelling is characteristic of all elastic materials but differs somewhat for different types of materials. A solid is said to swell when it takes up a liquid and at the same time fulfills the following 3 conditions (Nageli 1854): (a) Its dimensions are increased with an accompanying thermal change as a result of the taking up of another phase, (b) It retains its homogeneity in microscopic sense, (c) Its cohesion is diminished but not eliminated, that is, it becomes soft and flexible instead of hard and brittle. The swelling of wood with liquids is of fundamental significance to a wide range of commercial and experimental processes. It is encountered whenever a substance is added or removed from the cell wall in a wide variety of applications of wood. These include such diverse processes as pulping, preservation, removal of extractives, dimensional stabilization and chemical modification. Future uses of wood for modified products now under development will necessarily involve some type of chemical modification of wood. Also, further developments in the new solvent pulping processes will require more detailed information on the effect of organic liquids on wood.

Swelling of wood in organic liquids

Stamm and coworkers (Stamm 1935, 1964; Stamm and Tarkow 1950) evaluated the swelling of oven-dry white pine sections with a variety of organic liquids which had been carefully freed of water. Their results obtained with a series of aliphatic alcohols, esters and fatty acids demonstrated that the size of the molecule of the swelling liquid is an important consideration. An increase in size not only decreased the swelling rate but the swelling equilibrium was also decreased due to the greater difficulty for the larger molecules to diffuse into the fine capillary structure of wood and cellulose.

Schwalbe and Beiser (1931) studied the swelling of spruce wood in water and in aqueous solutions of several electrolytes. The wood showed an increase in volumetric swelling both in acids and bases and it differed from the swelling behavior of isolated spruce cellulose. Swelling measurements were carried out by measuring the changes in dimensions with a micrometer. As a result of an extensive investigation, these workers concluded that the swelling of wood in water and solutions of electrolytes was influenced by (a) the duration and method of drying, (b) the specific gravity of the wood, (c) the percentage of springwood and summerwood, and (d) the microscopic and macroscopic hairchecks in the wood.

Nayer (1948) performed the most thorough investigation on swelling of wood in organic liquids. He evaluated various possible predictive factors for wood swelling. He tried to correlate the volumetric swelling of thin-sections of wood in a large number of dry organic liquids against the dielectric constant, the dipole moment and the surface tension of the liquids. In general, poor correlations were obtained with the exception of benzene derivatives. In another publication, Nayer and Hossfeld (1949) concluded that a correlation existed between the degree of swelling and the extent of hydrogen bonding between the constituents of wood and the swelling agent. In addition, steric hindrance was suggested as a controlling influence on the intensity of the hydrogen bonding.

In early work, Hasseblatt (1926) also measured the maximum swelling of dried birchwood veneers in a variety of solvents. However, the organic liquids used by Hasseblatt were not free of water; and therefore, he reported erroneously high swelling values. The presence of water has been found to significantly influence the swelling of wood in many organic solvents.

Saechtting and Zocher (1934) extended the work of Hasseblatt by studying the swelling of sprucewood in benzene, ether, acetone, pyridine, methanol, and water. The volumetric swelling of sprucewood in benzene and ethyl ether was 5.13% and 2.79% respectively. The volumetric swelling of spruce in pyridine was 16.12% as compared to 14.83% for water. Thus, they showed that pyridine exerted a specific action on wood that might be attributed to its strong basic nature.

Ashton (1973) determined the effectiveness of dimethyl sulfoxide, dimethyl formamide, N-methyl pyrolidone and pyridine to swell yellow birch, beech, white pine and Douglas-fir wood. He found that birch was swollen the most by these solvents and pine the least, in relation to their densities. Also, beech and pine swelled more rapidly than Douglas-fir, which was the most resistant. Dimethylsulfoxide (DMSO) caused the greatest final swelling but dimethyl-formamide (DMF) swelled wood more rapidly. To swell wood effectively with DMSO required a vacuum impregnation process.

Kumar (1957, 1958) found a qualitative correlation between volumetric wood swelling and the amount of the liquid taken up under complete saturation. Also, he noted that an increase in the molecular size of the liquid in a homologous series of acids decreased the swelling in general and the swelling was also inversely proportional to the molecular weight of the impregnating liquid. The dimensions of the test wood specimens seemed to influence swelling in an irregular way.

Horiike and Kato (1959) suggested that a correlation existed between the degree of swelling and the heat of wetting of wood. The swelling behavior of the wood was explained by the hypothesis that the degree of swelling bears a direct relationship to the intensity of hydrogen bonding between the constituents of wood and the swelling agent. Kajita and coworkers (1979) showed that relationships existed between the total heat of wetting (W) and the physico-chemical parameters of 29 different organic solvents. In particular, a clear relationship existed between the W value and the hydrogen bonding capability of the solvents. Horiike and Kato (1959) also previously demonstrated a reasonably good correlation between swelling of wood and the W values of various organic solvents.

Rowell (1984), in an investigation on the reaction of epoxides with wood, observed the dramatic effect of temperature on wood swelling for a series of organic solvents. Some solvents which did not swell wood at room temperature were found to dramatically swell wood at elevated temperatures. West and Banks (West 1988; West and Banks 1989) in their thorough work measured rates of swelling of wood with temperature in a limited number of organic liquids. They assumed that the swelling was a bimolecular reaction merely requiring the collision of the solvent molecules with wood. They found that the rate of swelling in organic liquids showed a strong dependence on temperature which closely obeyed the classical Arrhenius equation (1889). Wood (Scots pine) swelling activation energies were calculated for a few solvents (KJ/mole): pyridine (46), acetone (48), quinoline (86) and pentanol (145). West proposed a “zipper” model for the movement of water and organic liquids (associated) such as pyridine into wood structure to cause swelling. However, application of their technique with water proved very difficult because of the very rapid swelling in water even at room temperature.

Mantanis *et al.* (1994) in their work on the swelling of wood in water, accurately evaluated, for the first time, activation energies of the wood swelling in water. Raising the water temperature above room temperature significantly increased the rate of swelling of wood. The activation energies obtained from Arrhenius plots ranged from 32.2 KJ/mole for sitka spruce to 47.6 KJ/mole for sugar maple. They also found that removal of “extractives caused a large decrease in the wood swelling activation energy, Ea.

The swelling of wood and wood polymers in liquids is a complex process which is strongly influenced by both the solvent and the wood substrate. Our broad investigation on swelling of wood is intended to ascertain the important factors to swelling in both water and organic liquids. In Part I, we evaluated the relative effects of factors such as wood density, extractives, and temperature to wood swelling in water. In this work, we have evaluated the influence of a wide variety of solvent factors such as molar volume, hydrogen bonding, basicity, dipole moment, dielectric constant, surface tension, etc., on the rate and maximum swelling of wood in organic solvents. In future publications, we will report on the activation energy of wood swelling in organic liquids (effects of temperature), the swelling of compressed fiber pellets in water and in various organic liquids as well as on the effect of extractives on the rate and maximum swelling of wood in some organic liquids.

Material and Methods

Material

Totally dry organic solvents were used in this study (with the exception of formic acid (96%), and quinoline (98%), which were not free of water). The organic solvents selected are representatives of various solvent chemical classes (Table 1). These organic liquids have different properties (hydrogen bonding parameter, molar volume, cohesive energy density, basicity, dipole moment, dielectric constant, volubility parameter, etc.). It is known that these solvent properties influence the wood swelling phenomenon in various ways. Therefore, their selection was chosen in such a way so that we were able to determine their relative effect on the swelling of wood.

Table 1. Solvents selected for wood swelling studies

Alcohols	Acids	Acetates	Aromatics
Methyl	Formic	Methyl	Toluene
Ethyl	Acetic	Ethyl	Benzaldehyde
Propyl	Propionic	Propyl	Nitrobenzene
Benzyl			

Nitrogen-containing	Others	
Diethylamine	Water	Acetone
Butylamine	Ethylene glycol	Dioxane
Dibutylamine	Formamide	2-Butanone
Pyridine	DMF	γ-Butyrolactone
2-Methylpyridine	DMSO	Furfural
2.6-Dimethylpyridine	Isopropyl ether	Octane
Quinoline	Chloroform	Butyraldehyde
Piperidine	Benzyl benzoate	Ethylene dichloride
Nitromethane	Carbon tetrachloride	
Pyrrole		

Heartwood samples of sitka spruce and Douglas-fir (softwoods), sugar maple and quaking aspen (hardwoods) were selected for this investigation. These wood species were selected as representative of softwoods and hardwoods with different compositions and densities. Their density varied from 0.4 to 0.7 gm/cc, and their extractives contents are very different. The samples were cut in the form of 25 (tangential) × 25 (radial) × 5 (longitudinal) mm pieces and oven-dried for 48 hours at 65°. Their average moisture content (MC) was 6-7% in the oven-dry basis. Sitka spruce *(Picea sitchensis* L.) had an average number of annual rings per cm of 10 in the air-dry state. The average specific gravity was 0.40. Sugar maple (*Acer saccharum* L.) had an average number of annual rings per cm from 5 to 7 in the air-dry state and the specific gravity varied from 0.69 to 0.71: the average was 0.70. Douglas-fir *(Pseudorsuga merrziesii* L.) had an average number of annual rings per cm from 3 to 8 in the air-dry state. Note that with Douglas-fir two different experiments were carried out; the first (Douglas-fir I) for wood samples having low densities (0.47-0.49) with an average of 3 to 4 rings/cm and another (Douglas-fir II) for wood samples having higher densities (0.57 to 0.60) with 7 to 8 rings/cm: quaking aspen *(Populus tremuloides* L.) had 6 to 8 annual rings per cm and the average specific gravity was 0.51. Only tangential swelling was measured. The longitudinal direction was chosen to be the shortest one (5 mm) to accomplish complete penetration of the liquids in a short time. Heartwood samples of the same wood species were cut in the form of 35 mm × 3 mm × 3 mm for the wood wetting measurements.

Methods

Two cross-sections each of spruce, fir, maple and aspen, prepared as described above, were swollen in 40 organic solvents at room temperature. All initial measurements were made at room temperature with a jaw-type vernier caliper, accurate to ±0.05 mm and with jaws sufficient to cover the full 25 mm block side of each wood sample. The oven-dry crow-sections were transferred from the oven and cooled in a desiccator. The cooled oven-dry weights and tangential dimensions were measured as quickly as possible. The maximum tangential swelling of the wood blocks in the dry organic liquids was determined in sealed weighing brittles placed in a thermostatically controlled bath (~23° C) for 100 days. The percentage swelling is calculated by the use of the equation:

$$\text{Percentage swelling} = \frac{(\text{Swollen Dim.} - \text{Oven Dry Dim.})}{(\text{Oven Dry Dimension})} \times 100 \quad (1)$$

The rate of wood swelling in all the organic solvents at room temperature was evaluated using a computerized linear variable displacement transformer (LVDT) apparatus previously described (Mantanis *et al.* 1994) with small intervals of time (15-600 see). Although a very small induction period is anticipated, the slope of the initial linear portion of the plot of tangential swelling with time (Figs. 1, 2a, b) was used as the estimate of the swelling rate, k (tangential % per minute).

Contact angle measurements were done by the Wihelmy method based on the equation:

$$F = \gamma_{LV}\, P \cos\theta$$

where F is the force, γ_{LV} is the liquid surface tension. P is the sample perimeter; the latter two values were obtained by independent measurement, which gives the contact angle, θ .

The work of adhesion was then obtained from the equation:

$$W_A = \frac{F}{P} + \gamma_{LV} = \gamma_{LV}\,(1 + \cos\theta)$$

The Wilhelmy technique was not widely utilized until sensitive microbalances were developed which allowed reproducible, quantitative force measurements on rods and fibers (Young 1976). The method involves suspension of a small, end-sealed (adhesive) wood sample in a liquid and measurement of the force of the interaction on a microbalance. The weight force is obtained by measuring the apparent weight increase when the wood sample contacts a liquid of known surface tension. However, a variety of secondary forces have been implicated in wetting. Therefore, additional information can be obtained by measuring the relative contributions of these secondary forces; dispersive, polar, hydrogen bonding, acid-base to the overall work of adhesion. For simplicity, work of adhesion can be written by considering only the two components, dispersion and polar forces.

$$W_A = W_A^{d} + W_A^{p}$$

However, Fowkes (1962) has suggested that the polar forces are very small and can be considered as negligible and hydrogen bonding is a form of acid-base interactions such that.

$$W_A = W_A^d + W_A^{ab}$$

If it is accepted that the dispersive components of the surface free energy interact according to a geometric mean square, then

$$W_A^d = 2\,(\gamma_S^d \gamma_{LV}^d)^{1/2} = \gamma_L\,(1 + \cos\theta)$$

If we consider that the adsorption of the vapor of the probe liquid is negligible, then the dispersive component is obtained from the equation.

$$\gamma_S^d = \gamma_{LV}\,(1 + \cos\theta)^2 / 4$$

Methylene iodide was used as dispersive probe liquid to obtain γ_s^d. Hence, the acid-base contributions to the work of adhesion can be determined using formamide or ethylene glycol as Lewis base and acid probes, respectively, and from the previous equation rewritten as,

$$W_A^{ab} = W_A - W_A^d$$

All wetting force measurements were performed with a CAHN Dynamic Contact Angle Analyzer by attaching a wood sample to the electrobalance and raising a beaker of wetting liquid with a small elevator until the liquid contacts the sample. The elevator speed was controlled at 100 microns per second and force readings were obtained on a microcomputer. Hexadecane, which has very low surface tension, was chosen for measuring the sample perimeter. Average 'advancing' force values minus the buoyancy force were then used to calculate the work of adhesion and contact angles.

Results and Discussion

Figure 1 is a typical plot of the swelling of quaking aspen in pyridine at room temperature (23 °C). The percent tangential swelling is plotted against time (min). The maximum equilibrium swelling is reached after about 7 hours of swelling. Figure 2 a is a detailed plot of the initial linear portion of the Figure 1 (aspen in pyridine at 23 °C) but at an interval time of two minutes. An induction period of 5–6 min is noted in this case. In general, a small induction period was noted in most of the swelling profiles. This period was also noted by West (1988) in his study of the swelling of wood in organic liquids. The induction period is probably related to the time necessary for the initial diffusion of the liquid into the cell wall structure of the wood. However, West (1988) has suggested that the induction period reflects a gradual increase in the number of cell wall capillaries that participate in the swelling process as the liquid moves from the lumen into the cell wall and progresses slowly along in the fiber direction. To accommodate this induction period, West and Banks (1989) calculated a time to one-half swell (t 1/2). In contrast, in this work, the initial linear slope of the swelling profile was taken as an estimate of the wood swelling rate (Figs. 1, 2a, b). Similarly, Stamm (1956) in his work on the diffusion of liquids into cellulosic materials noticed that, characteristically after the induction period, the initial 2/3 portion

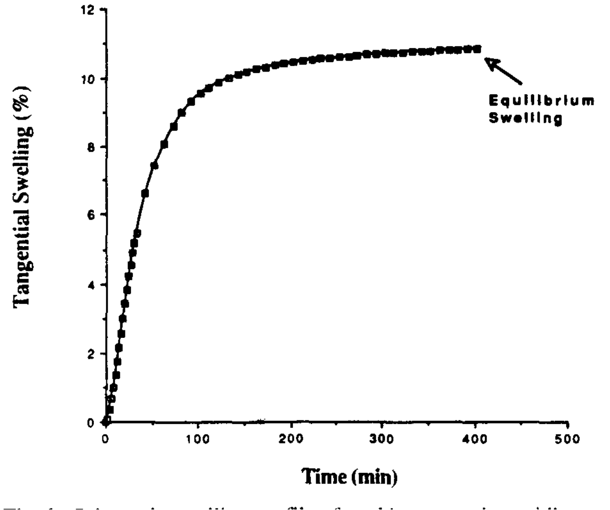

Fig. 1. Schematic swelling profile of quaking aspen in pyridine at 23 °C.

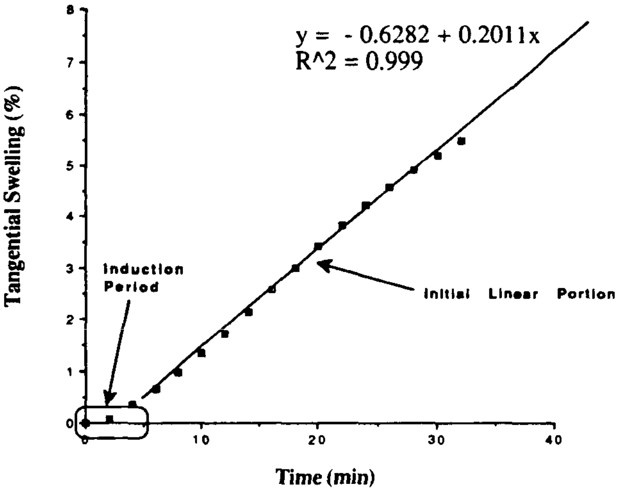

Fig. 2a. Initial linear swelling of quaking aspen in pyridine at 23 °C.

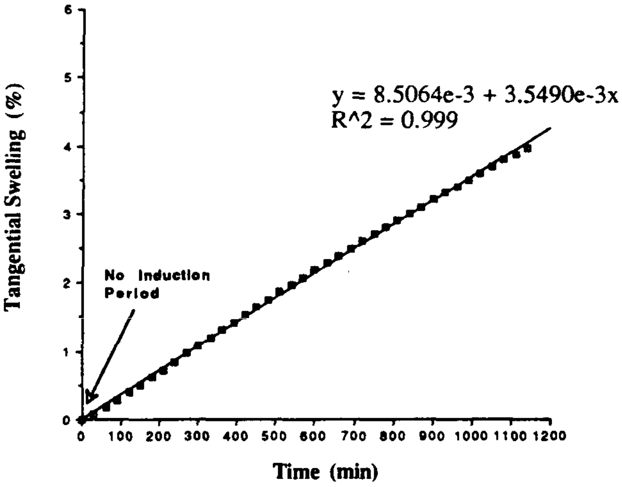

Fig. 2b. Initial linear swelling of Douglas-fir II (higher density) in ethylene glycol at 23 °C.

of the tangential swelling profile of sprucewood in water produced a straight line relationship. A swelling rate constant, k, is then derived from the slope of this curve (k= 0.2011 %/min). Figure 2b is another example of this initial swelling profile, in this case, for Douglas-fir II in ethylene glycol at room temperature (k= 0.0035 %/min). However, no induction period was noted in this case. Similar measurements were made for wood in all forty solvents at room temperature.

Maximum swelling of wood in organic solvents

The data presented in Table 2 show the maximum tangential swelling of all wood species in the anhydrous organic solvents at the end of 100 days. The standard deviations are presented in the parentheses. In general, no large deviations were observed. Results indicate that formic acid, butylamine, dimethylformamide, pyridine, formamide, dimethylsulfoxide, diethylamine, and 2-methylpyridine swell all the wood species beyond the water-swollen dimensions. The largest amount of wood swelling was caused by formic acid and butylamine (all species). However, it should be stressed that formic acid was not free of water (96%). Much lower swelling values would be expected for wood swelling in anhydrous formic acid. Quinoline, octane, butyraldehyde, nitrobenzene, carbon tetrachloride, benzyl benzoate, and piperidine

Table 2. Maximum tangential swelling of wood at 23 °C at the end of 100 days

		Sitka spruce		Douglas-fir I		Douglas-fir II		Sugar maple		Quaking aspen	
		(Standard deviations in parentheses)									
Class I	Water	8.4	(0.2)	8.8	(0.1)	10.0	(0.3)	10.6	(0.3)	8.9	(0.3)
	Formamide	11.2	(0.3)	9.6	(0.2)	11.3	(0.2)	16.8	(0.4)	12.0	(0.3)
	Ethylene glycol	9.5	(0.2)	9.1	(0.1)	11.6	(0.2)	10.4	(0.3)	10.1	(0.2)
	Methanol	8.2	(0.3)	7.3	(0.2)	9.2	(0.1)	8.7	(0.2)	8.4	(0.2)
	Ethanol	7.0	(0.2)	6.3	(0.2)	7.3	(0.2)	6.9	(0.1)	7.7	(0.3)
	Propanol	4.9	(0.1)	5.1	(0.2)	6.6	(0.1)	5.3	(0.2)	6.0	(0.2)
Class II	DMF	11.8	(0.3)	11.5	(0.4)	14.7	(0.4)	13.2	(0.4)	13.2	(0.3)
	Pyridine	12.2	(0.4)	11.4	(0.4)	15.0	(0.4)	13.3	(0.3)	12.1	(0.3)
	Acetone	5.7	(0.2)	4.6	(0.2)	7.2	(0.3)	7.1	(0.2)	7.5	(0.2)
	2-Butanone	4.3	(0.4)	4.1	(0.3)	5.6	(0.3)	5.1	(0.2)	6.0	(0.2)
	Dioxane	5.7	(0.2)	7.5	(0.3)	8.9	(0.2)	8.4	(0.3)	9.1	(0.3)
	Ethylacetate	2.6	(0.3)	2.7	(0.3)	2.6	(0.1)	3.7	(0.1)	5.5	(0.1)
	Butyraldehyde	0.7	(0.2)	0.66	(0.1)	0.84	(0.1)	1.21	(0.1)	3.4	(0.0)
	Methylacetate	5.0	(0.3)	4.7	(0.2)	5.2	(0.3)	5.6	(0.1)	5.7	(0.1)
	Propylacetate	2.2	(0.1)	1.4	(0.2)	1.7	(0.2)	3.1	(0.2)	4.9	(0.2)
Class III	Nitromethane	4.5	(0.1)	4.0	(0.1)	4.6	(0.2)	5.4	(0.1)	6.0	(0.1)
	Butyrolactone	7.2	(0.2)	7.5	(0.0)	8.6	(0.2)	9.6	(0.2)	9.2	(0.1)
	Furfural	5.5	(0.1)	5.4	(0.2)	5.7	(0.1)	7.6	(0.2)	7.8	(0.3)
Class IV	Chloroform	1.4	(0.1)	1.5	(0.1)	1.7	(0.1)	3.9	(0.3)	5.5	(0.1)
	Ethylene dichloride	2.1	(0.2)	2.1	(0.1)	2.4	(0.2)	4.6	(0.2)	5.0	(0.2)
	Carbon tetrachloride	1.2	(0.1)	1.3	(0.0)	1.4	(0.1)	1.1	(0.1)	1.2	(0.0)
Class V	Benzaldehyde	1.0	(0.1)	0.9	(0.1)	1.2	(0.1)	2.1	(0.0)	6.1	(0.2)
	Nitrobenzene	0.5	(0.0)	0.4	(0.0)	0.56	(0.0)	0.72	(0.1)	2.1	(0.0)
	Toluene	1.6	(0.2)	1.5	(0.2)	1.7	(0.1)	1.5	(0.0)	1.6	(0.1)
	Isopropyl ether	1.5	(0.1)	1.3	(0.1)	1.5	(0.1)	1.0	(0.1)	1.3	(0.1)
	Benzyl alcohol	2.9	(0.2)	2.6	(0.1)	2.2	(0.1)	8.9	(0.1)	9.6	(0.2)
	Quinoline (98%)	0.37	(0.0)	0.29	(0.0)	0.56	(0.1)	0.56	(0.0)	2.4	(0.1)
	Octane	0.85	(0.0)	0.72	(0.0)	0.64	(0.0)	0.6	(0.0)	0.8	(0.1)
Others	Pyrrole	7.6	(0.2)	6.9	(0.2)	7.8	(0.2)	12.0	(0.2)	10.1	(0.2)
	DMSO	13.9	(0.3)	13.7	(0.1)	16.7	(0.4)	14.5	(0.3)	14.4	(0.2)
	Benzyl benzoate	1.0	(0.0)	0.9	(0.2)	1.1	(0.0)	1.0	(0.1)	0.9	(0.0)
Acids	Formic (96%)	14.9	(0.1)	17.4	(0.2)	21.4	(0.1)	20.3	(0.3)	17.0	(0.3)
	Acetic	8.7	(0.1)	7.6	(0.2)	9.3	(0.0)	10.2	(0.2)	11.6	(0.2)
	Propionic	6.4	(0.2)	6.3	(0.0)	7.2	(0.1)	10.0	(0.1)	8.0	(0.1)
Amines	2.6-Dimethylpyridine	1.3	(0.1)	1.0	(0.0)	1.1	(0.1)	6.3	(0.1)	8.1	(0.1)
	Diethylamine	10.1	(0.3)	10.4	(0.1)	12.4	(0.2)	11.0	(0.2)	10.6	(0.2)
	Butylamine	14.5	(0.0)	16.4	(0.2)	21.1	(0.3)	19.3	(0.2)	18.2	(0.2)
	Dibutylamine	1.3	(0.0)	1.0	(0.0)	1.1	(0.1)	0.8	(0.1)	0.9	(0.0)
	2-Methylpyridine	10.8	(0.1)	11.6	(0.1)	12.8	(0.1)	11.9	(0.1)	11.7	(0.0)
	Piperidine	0.9	(0.0)	0.62	(0.0)	0.6	(0.0)	4.3	(0.1)	12.3	(0.1)

(softwoods) exhibited the lowest maximum tangential swelling values. In general, the hardwoods, maple and aspen, swelled to a much greater extent compared with the softwoods, spruce and Douglas-fir. This is very likely due to the greater density of the hardwoods (Mantanis *et al.* 1994).

Table 3 shows the maximum tangential swelling values relative to that in water. Most organic liquids seem to swell the various wood species to an almost consistent extent, however variations among the wood species did occur. Exceptions included piperidine. 2.6 lutidine, benzaldehyde, benzyl alcohol, butyraldehyde, This may be due to the extremely slow rate of swelling of the softwoods in these solvents, that is, swelling at the end of 100 days probably was not the final equilibrium swelling. Overall, the swelling results are in a very good agreement with Nayer's (1948) and Stamm's (1964) work. From Tables 2 and 3, the pronounced swelling effect that the primary amines have on wood is obvious. The lower amines swelled wood relatively fast while the higher (bulkier) ones extremely slowly. The maximum swelling observed in the homologous series of alcohols is in a descending order (Water > MeOH > EtOH > PrOH), a result demonstrated by previous investigators (Stamm 1935; Stamm 1964). The same pattern is followed for the maximum swelling in the homologous series of organic acids (Fig. 3) and acetates (Fig. 4). It is apparent that as the solvent molecule becomes bulkier, the wood

Table 3. Maximum tangential swelling relative to that in water at 23 °C

		Sitka spruce	Douglas-fir I	Douglas-fir II	Sugar maple	Quaking aspen
	Water	100.0	100.0	100.0	100.0	100.0
Class I	Formamide	133.3	109.1	113.0	158.5	134.8
	Ethylene glycol	113.1	103.4	116.0	98.1	113.5
	Methanol	97.6	83.0	92.0	82.1	94.4
	Ethanol	83.3	71.6	73.0	65.1	86.5
	Propanol	58.3	58.0	66.0	50.0	67.4
Class II	DMF	140.5	130.7	147.0	124.5	148.3
	Pyridine	145.2	129.5	150.0	125.5	136.0
	Acetone	67.9	52.3	72.0	67.0	84.3
	2-Butanone	51.2	46.6	56.0	48.1	67.4
	Dioxane	67.9	85.2	89.0	79.2	102.2
	Ethylacetate	31.0	30.7	26.0	34.9	61.8
	Butyraldehyde	8.3	7.5	8.4	11.4	38.2
	Methylacetate	59.5	53.4	52.0	52.8	64.0
	Propylacetate	26.2	15.9	17.0	29.2	55.1
Class III	Nitromethane	53.6	45.5	46.0	50.9	67.4
	Butyrolactone	85.7	85.2	86.0	90.6	103.4
	Furfural	65.5	61.4	57.0	71.7	87.6
Class IV	Chloroform	16.7	17.0	17.0	36.8	61.8
	Ethylene dichloride	25.0	23.9	24.0	43.4	56.2
	Carbon tetrachloride	14.3	14.8	14.0	10.4	13.5
Class V	Benzaldehyde	11.9	10.2	12.0	19.8	68.0
	Nitrobenzene	6.0	4.5	5.6	6.8	23.6
	Toluene	19.0	17.0	17.0	14.2	18.0
	Isopropyl ether	17.9	14.8	15.0	9.4	14.6
	Benzyl alcohol	34.5	29.5	22.0	84.0	107.9
	Quinoline	4.4	3.3	5.6	5.3	27.0
	Octane	10.0	8.0	7.0	5.5	9.0
Others	Pyrrole	90.5	78.4	78.0	113.2	113.5
	DMSO	165.5	155.7	167.0	136.8	161.8
	Benzyl benzoate	11.9	10.2	11.0	9.4	10.1
Acids	Formic	177.4	197.7	214.0	191.5	191.0
	Acetic	103.6	86.4	93.0	96.2	130.3
	Propionic	76.2	71.6	72.0	94.3	89.9
Amines	2.6-Dimethylpyridine	15.0	11.0	11.0	59.0	91.0
	Diethylamine	120.2	118.2	124.0	103.8	119.1
	Butylamine	172.6	186.4	211.0	182.1	204.5
	Dibutylamine	15.5	11.4	11.0	7.5	10.1
	2-Methylpyridine	128.6	131.8	128.0	112.3	131.5
	Piperidine	10.7	7.0	6.0	40.6	138.2

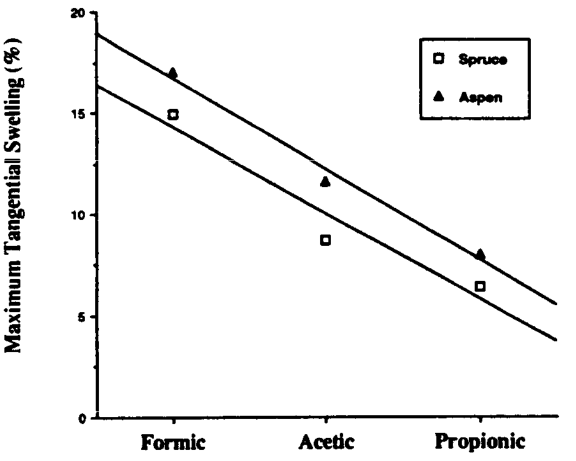

Fig. 3. Maximum tangential swelling of wood in organic acids. Note: each point is the average of 2 replicates.

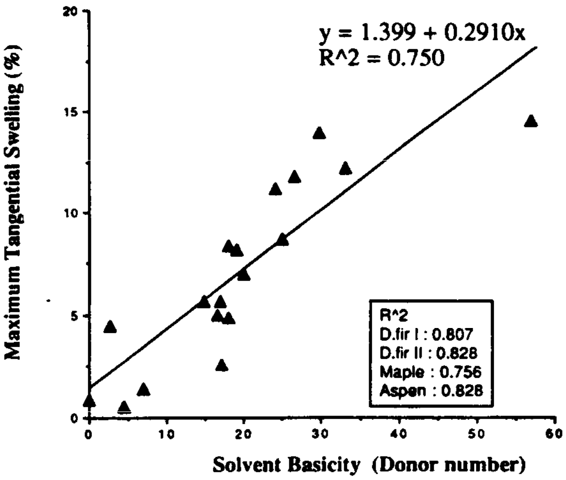

Fig. 5. Maximum tangential swelling of sitka spruce plotted against solvent basicity. (DN data available for 18 of our solvents.)

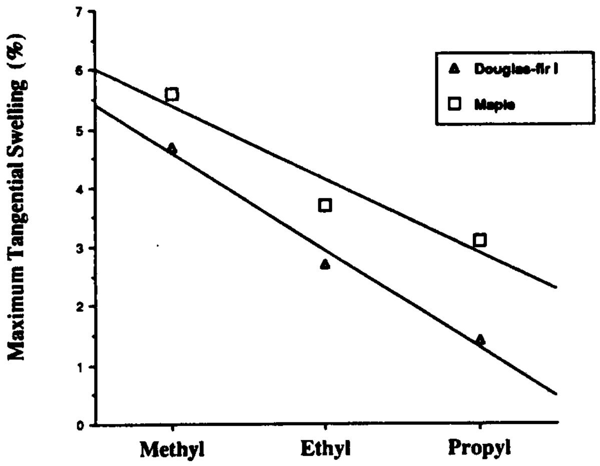

Fig. 4. Maximum tangential swelling of wood in acetates. Note: Each point is the average of 2 replicates.

maximum swelling decreases constantly (within a homologous series). In Figure 3, the maximum for formic acid would be expected to occur at a lower level if the formic acid were anhydrous.

None of the typical solvent properties such as solubility parameter, dielectric constant, dipole moment, and surface tension showed any consistent correlation with the maximum swelling of wood. This was true for all the wood species. However, a correlation was found between the maximum tangential swelling and the solvent donor number (Fig. 5). Donor number (DN) was introduced by Gutmann (1976) to describe the nucleophilic behavior or donicity of a particular solvent (solvent basicity). Simply defined, donicity is the negative AH-value in kcal/mol for the interaction of an electron pair donor solvent (EPD) with $SbCl_5$ in a highly diluted solution of dichloroethane. However, solvent basicity data are available for only a limited number of solvents, therefore, we correlated only 18 solvents with DN data for the maximum wood swelling (Fig. 5). In general, very strong relationships were obtained. However, this linear relationship was expected since wood by nature has an acidic character (Wood pH = 4.0-6.0) (Fengel and Wegener 1984). Wetting force measurements of the wood samples by the Wilhelmy technique also clearly show that wood has acidic character. As shown in Table 4, the greatest interactions for all the wood samples occur with the basic probe, formamide, while lower readings are obtained with the acidic probe, ethylene glycol. This may also explain why amines are generally excellent wood swelling agents; because of their strong basic nature.

Rate of swelling of nood in organic liquids

In Table 5 the rates of swelling of wood in all the organic liquids at 23 °C are presented in units of tangential % per minute. It is obvious from Table 5 that some organic solvents swell wood at an extremely slow rate. Such solvents include piperidine, dibutylamine, 2,6 dimethylamine, quinoline, benzyl benzoate, benzyl alcohol, isopropyl ether, toluene, nitrobenzene, benzaldehyde, carbon tetrachloride, ethylene dichloride, chloroform, propyl acetate, and butyraldehyde. The fastest swelling rates were ob-

Table 4. Work of adhesion of wood with various liquid probes

Species	Water (bi-functional) Wa. (dynes/cm) (Θ)	Ethylene glycol (acidic) Wa (ab) (dynes/cm)	Formamide (basic) Wa (ab) (dynes/cm)
Spruce	108.2 (60.4)	21.2	30.6
Douglas-fir	93.2 (73.5)	16.5	34.3
Maple	106.6 (62.2)	24.4	29.5
Aspen	99.7 (68.2)	12.7	20.3

tained with methanol, ethanol, water, butylamine, formic acid, DMF, formamide, and DMSO. It is also noted that the wood swelling rate increased dramatically with the smallest molecule in each of the homologous series of alcohols, acetates, and organic acids as previously noted. This was anticipated due to the greater difficulty for the larger molecules to diffuse into the fine capillary structure of wood (Stamm 1964). Solvents that swelled wood faster than water were, methanol (spruce, Douglas-fir I, and aspen), butylamine (aspen), and formic acid (spruce, Douglas-fir I, and aspen). Of course the presence of water in the formic acid would act as a promoter for the wood swelling process. A comparison of the wood swelling rates in pyridine, 2-methylpyridine, and 2,6 dimethylpyridine shows that, for all wood species, the addition of the methyl group retards significantly the rate of the swelling. This is also attributable to the increased molecular size and associated steric effects in comparison to butylamine and dibutylamine.

Correlations were also attempted between swelling rate and molecular weight, molar volume, and maximum swelling. We concluded that there was a clear inverse correlation between the logarithm of the rate of wood swelling and the molecular weight of the swelling liquid (Fig. 6). This trend was consistent for all wood species. In addition, a consistent trend was

Table 5. Rates of swelling of wood in 40 organic solvents at room temperature

		Rate of swelling of wood. k = Initial linear slope (% per min)				
		Sitka spruce	Douglas-fir I	Douglas-fir II	Sugar maple	Quaking aspen
Class I	Water	9.8 e-1	3.0 e-1	7.0 e-1	3.0 e-1	8.0 e-1
	Formamide	2.8 e-1	9.9 e-2	5.9 e-2	1.8 e-1	4.8 e-2
	Ethylene glycol	6.0 e-3	3.3 e-3	3.6 e-3	1.3 e-3	5.3 e-3
	Methanol	2.0 e+0	7.9 e-1	3.5 e-1	1.9 e-1	1.4 e+0
	Ethanol	1.3 e-1	4.0 e-2	3.0 e-2	6.0 e-2	2.5 e-1
	Propanol	4.3 e-4	4.2 e-4	1.3 e-4	6.9 e-4	1.4 e-2
Class II	DMF	2.9 e-1	1.0 e-1	9.2 e-2	9.1 e-2	2.0 e-1
	Pyridine	7.8 e-3	7.5 e-3	9.4 e-3	6.0 e-3	2.0 e-1
	Acetone	3.5 e-3	2.1 e-3	1.9 e-3	1.7 e-2	2.3 e-1
	2-Butanone	4.1 e-4	2.2 e-4	4.8 e-5	4.4 e-3	1.9 e-2
	Dioxane	5.4 e-5	5.6 e-5	4.1 e-5	2.2 e-4	1.2 e-3
	Ethylacetate	3.4 e-5	5.9 e-5	5.5 e-5	5.6 e-4	3.0 e-3
	Butyraldehyde	4.2 e-6	4.7 e-6	5.6 e-6	5.4 e-6	1.9 e-5
	Methylacetate	2.0 e-3	9.6 e-4	2.1 e-4	2.2 e-2	7.8 e-2
	Propylacetate	1.9 e-5	2.1 e-5	1.7 e-5	6.2 e-5	2.9 e-4
Class III	Nitromethane	4.5 e-3	4.0 e-3	1.5 e-3	1.6 e-2	1.0 e-1
	Butyrolactone	1.4 e-4	2.0 e-4	1.0 e-4	2.6 e-4	7.1 e-3
	Furfural	1.7 e-4	1.3 e-4	1.0 e-4	8.9 e-4	7.1 e-3
Class IV	Chloroform	2.6 e-5	2.6 e-5	3.6 e-5	1.3 e-4	1.6 e-3
	Ethylene dichloride	1.9 e-5	1.4 e-5	1.9 e-5	7.9 e-5	1.0 e-3
	Carbon tetrachloride	1.0 e-5	8.3 e-6	9.9 e-6	1.1 e-5	1.4 e-5
Class V	Benzaldehyde	9.7 e-6	8.8 e-6	7.7 e-6	3.0 e-5	6.4 e-5
	Nitrobenzene	8.4 e-5	4.8 e-6	3.8 e-6	6.4 e-6	1.7 e-5
	Toluene	1.1 e-5	9.8 e-6	1.1 e-5	1.2 e-5	1.5 e-5
	Isopropyl ether	1.1 e-5	1.0 e-5	1.0 e-5	1.1 e-5	1.4 e-5
	Benzyl alcohol	2.6 e-5	2.1 e-5	1.9 e-5	5.0 e-5	1.7 e-4
	Quinoline	4.7 e-6	5.1 e-6	3.9 e-6	4.6 e-6	1.9 e-5
	Octane	8.1 e-6	9.4 e-6	1.1 e-5	7.3 e-6	2.0 e-5
Others	DMSO	1.3 e-1	4.9 e-2	2.4 e-2	1.7 e-2	2.8 e-1
	Pyrrole	2.0 e-4	9.5 e-5	5.7 e-5	1.0 e-2	3.5 e-2
	Benzyl benzoate	6.9 e-6	6.7 e-6	8.5 e-6	9.1 e-6	6.3 e-6
Acids	Formic	1.5 e+0	5.8 e-1	4.4 e-1	1.6 e-1	1.7 e+0
	Acetic	1.8 e-2	6.4 e-3	5.0 e-3	5.3 e-2	1.9 e-1
	Propionic	2.5 e-4	4.7 e-4	3.1 e-4	4.7 e-3	1.2 e-2
Amines	2.6-Dimethylpyridine	6.8 e-6	8.8 e-6	1.1 e-5	6.7 e-5	8.7 e-5
	Diethylamine	6.4 e-4	7.1 e-4	1.1 e-3	3.5 e-3	3.8 e-2
	Butylamine	5.2 e-1	2.5 e-1	1.2 e-1	4.9 e-2	1.6 e+0
	Dibutylamine	1.1 e-5	8.8 e-6	8.2 e-6	1.1 e-5	7.7 e-6
	2-Methylpyridine	3.0 e-4	2.3 e-4	5.9 e-5	5.2 e-3	4.2 e-2
	Piperidine	1.5 e-5	7.6 e-6	7.6 e-6	4.6 e-5	2.7 e-4

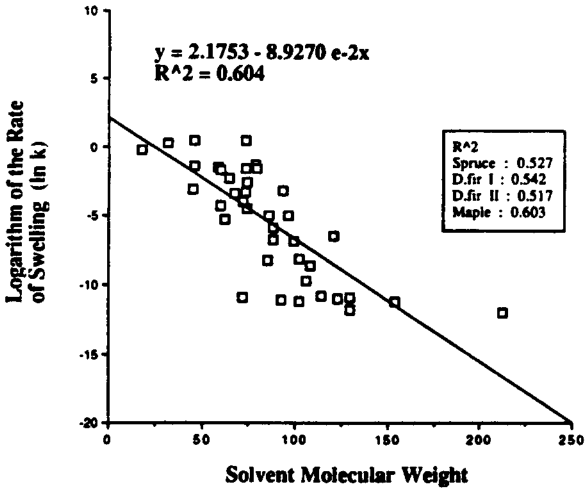

Fig. 6. The logarithm of the rate of swelling of aspen plotted against the solvent molecular weight.

found between the ln k and the molar volume of the swelling solvent (Fig. 7). Figure 7 represents clear graphical evidence of the importance of molecular size of the solvent, as a significant wood swelling rate-determining factor. Squares of the regression coefficients of the trends for the other wood species are also shown in Figure 7. In Figure 8, a strong relationship between ln k and maximum tangential swelling of wood is illustrated. This indicates that, in general, the faster the swelling rate the higher the final maximum swelling.

Cellulose versus wood maximum swelling

A physical classification of the organic liquids used in this work is given in Table 6. We divided the swelling liquids into five chemical classes with the classification based on three solvent properties (molar volume, hydrogen bonding parameter, and

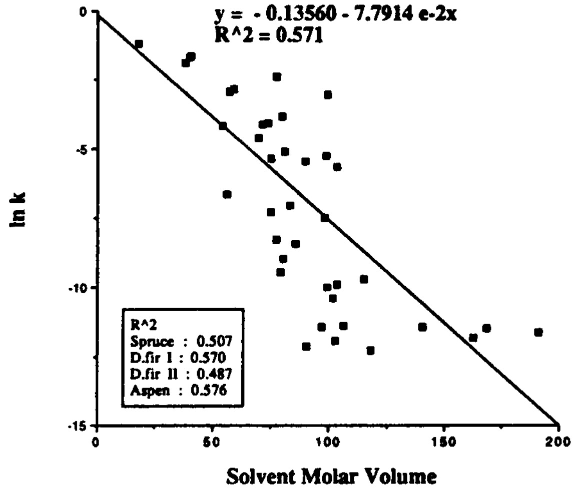

Fig. 7. The logarithm of the rate of swelling of maple plotted against the solvent molecular volume.

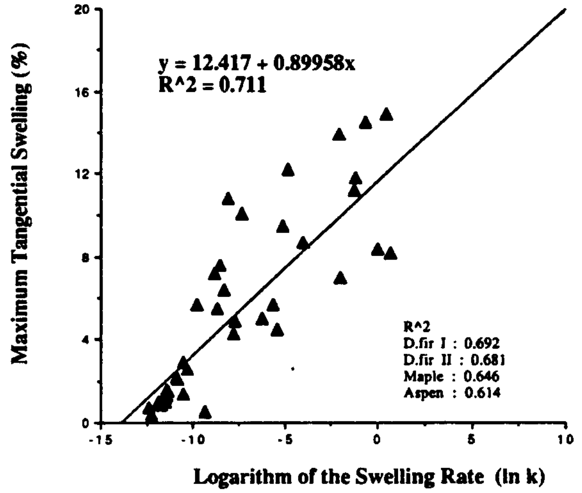

Fig. 8. The maximum tangential swelling of spruce plotted against ln k.

Table 6. Chemical classification of organic liquids

Class I		Class II		Class III		Class IV		Class V	
High CED[a] Low molar volume Hydrogen bonds		Medium CED Low molar volume Hydrogen bonds		High CED Low molar volume No hydrogen bonds		Low CED Low molar volume no hydrogen bonds		Molar volume Greater than 100cc	
Water	[b](H)	DMF	(H)	Nitromethane	(L)	Chloroform	(L)	Benzaldehyde	(M)
Formamide	(H)	Pyridine	(H)	Butyrolactone	(M)	Ethylene dichloride	(L)	Nitrobenzene	(L)
Methanol	(H)	Acetone	(M)	Furfural	(L)	Carbon tetrachloride	(L)	Toluene	(L)
Ethanol	(H)	2-Butanone	(M)					Isopropyl ether	(M)
Propanol	(H)	Dioxane	(M)					Benzyl alcohol	(H)
Ethylene glycol	(H)	Methyl acetate	(M)					Quinoline	(H)
		Ethyl acetate	(M)					Octane	(L)
		Propyl acetate	(M)						
		Butyraldehyde	(M)						

[a] CED = Cohesive Energy Density (Hansen 1967). [b] Hydrogen Bonding Parameter (H)= high: (M)= medium: (L)= low: all acids and amines have a high HB parameter (Liebermann 1962).

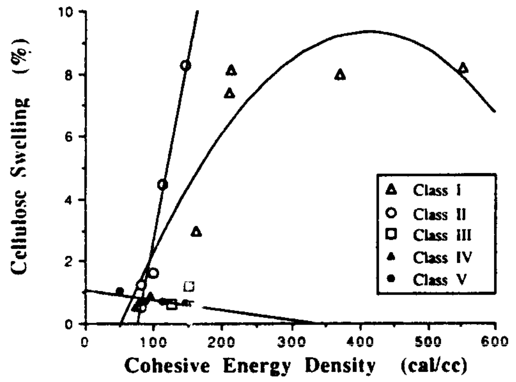

Fig. 9. Cellulose swelling versus solvent CED within various solvent classes (Data taken from Robertson, 1964).

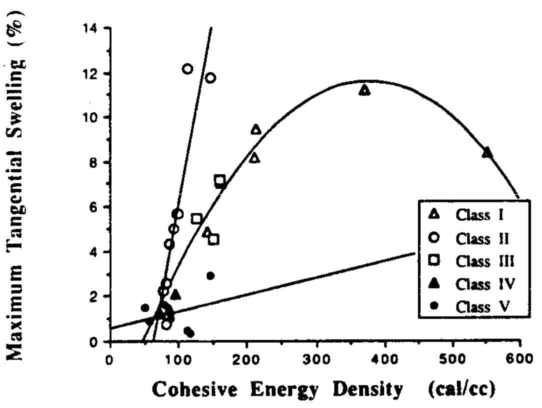

Fig. 10. Sitka spruce swelling vs. solvent CED within various solvent classes.

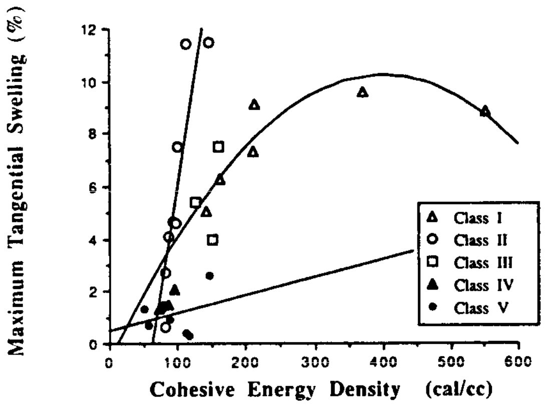

Fig. 11. Douglas-fir I swelling vs. solvent CED within various solvent classes.

cohesive energy density). Robertson (1964) evaluated the swelling of cellulose in five similar chemical classes. His swelling results for cellulose are plotted in Figure 9. None of the liquids of the classes III. IV, and V swelled cellulose to any appreciable extent. Our results for swelling of spruce and Douglas-fir I with the same classes of solvents follow the same pattern (Figs. 10, 11). Very similar results were also found for the other three wood species. In general, all the solvents with a molar volume > 100 cc or a low hydrogen bonding parameter showed very low wood swelling, with the exception of nitromethane and furfural which exhibited a medium wood swelling ability (4–6%). Notable is the swelling behavior of benzyl alcohol for hardwoods; although its molar volume is very high, its strong swelling ability is explainable by its very high hydrogen bonding capability. The apparent similarities found between cellulose and maximum swelling indicate that the cellulose polymer is probably primarily responsible for the maximum wood swelling.

Previous workers (Nayer 1940: Stamm 1964) have shown that the swelling behavior of wood is fairly predictable from the intensity of the hydrogen bonding capability of the swelling solvent. Indeed, a similar trend was shown from our results, with the exceptions of solvents such as quinoline, benzaldehyde, butyraldehyde, isopropyl ether, dibutylamine, and piperidine which showed once again that other factors such as molar volume, solvent basicity, steric hindrance, molecular branching must also be taken into account. Nevertheless, this strong correlation between the hydrogen bond breaking mechanism for wood swelling. A bimolecular process is most likely, whereby the solvent forms a transition state then collapses to give a molecule of liquid attached by a hydrogen bond to wood. In general, liquids with a strong hydrogen bonding parameter (HB), would be expected to swell wood to the greatest extent. Indeed, Figure 12 clearly shows that solvents with a high HB swelled wood more than those of a medium or low HB. This is true for all wood species. Each column represents the average maximum swelling in each solvent class (high, medium, and low HB) within the same wood species.

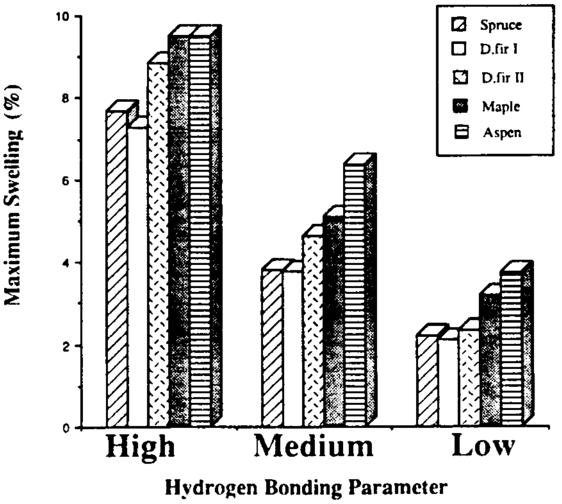

Fig. 12. The effect of the solvent hydrogen bonding capability on the maximum tangential swelling of wood.

Conclusions

The rates of swelling of four wood species in forty organic liquids at room temperature have been obtained. The logarithm of the rate of wood swelling was inversely correlated with the molecular weight (MW) and the molar volume (MV) of the swelling liquid, and linearly with the maximum tangential swelling of wood at the end of 100 days. The maximum swelling of wood in organic solvents is mainly influenced by three solvent properties, the solvent basicity, the molar volume, and the hydrogen bonding capability. In addition, strong similarities were found between wood and cellulose maximum swelling behavior in various organic solvent classes. Consequently, it is suggested that cellulose is the major polymer responsible for wood swelling.

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