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Swelling of Wood

Part III. Effect of Temperature and Extractives on Rate and Maximum Swelling

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Keywords

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Sitka spruce
Douglas-fir
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Summary

The swelling of wood in organic liquids at elevated temperatures has been investigated with the use of a computerized linear variable displacement transformer (LVDT). Wood swelled extremely fast at high temperatures. The rate of wood swelling in organic liquids showed a strong dependence on temperature which closely obeyed the classical Arrhenius equation. This strict linear dependence of wood swelling on the temperature clearly suggests a chemical mechanism. Activation energies for wood swelling (E_a) in several chemical classes of organic liquids have been obtained from Arrhenius equation plots. A strong linear relationship was found to exist between E_a and solvent molecular weight. Removal of extractives greatly enhanced the maximum tangential swelling of wood, especially for sugar maple. There was also a significant increase in the wood swelling rate after removal of extractives.

Introduction

The swelling of wood in water and organic liquids is of significant importance. Most of the previous work has been directed towards the extent of wood swelling at equilibrium (Saechtting and Zocher 1934; Stamm 1935; Stamm and Loughborough 1942; Nayer 1948; Stamm 1956; Kumar 1957; Ashton 1973; Ishimaru 1988). In this work, the rate of wood swelling has been investigated, and the effect of temperature as well as the effect of extractives on the rate and maximum swelling of wood have also been ascertained.

Effect of temperature on wood swelling

Rowell and Ellis (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 liquids. Some liquids which did not swell wood at room temperature were found to dramatically swell wood at elevated temperatures.

West (1988) found that quinoline could swell wood to about the same extent as water, but only when the temperature was raised considerably above room temperature. In further work, West and Banks (1989) found that the rate of wood swelling in a limited number of organic liquids showed a strong dependence on temperature which closely obeyed the classical Arrhenius equation. Wood (Scots pine) swelling activation energies were calculated for a few solvents (KJ/mole): pyridine (46), acetone (48), quinoline (86) and pentanol (145). They assumed that wood

swelling was a bimolecular reaction merely requiring the collision of liquid molecules with wood. West (1988) 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.* (1994a) accurately evaluated, for the first time, activation energies for wood swelling in water using a computerized linear variable displacement transformer. They obtained activation energies for wood swelling in water from Arrhenius plots, which ranged from 32.2 KJ/mole for sitka spruce to 47.6 KJ/mole for sugar maple. In another publication, Mantanis *et al.* (1994b) evaluated rates of wood swelling in forty organic liquids at room temperature. They showed that strong correlations existed between wood swelling rate and molar volume, molecular weight, and maximum tangential swelling. The maximum swelling of wood was mainly influenced by three solvent properties; basicity (donor number), molecular volume, and a hydrogen bonding parameter. They also suggested that cellulose is the primary wood polymer responsible for the major amount of wood swelling.

Effect of extractives on wood swelling

Some wood constituents can be extracted with organic liquids such as ethanol, acetone, etc. These components include resin acids, fats, terpenes, lignans, flavonoids, tannins, stilbenes, etc. (extractives).

The content of extractives and their composition vary greatly among different wood species and also within the different parts of the same tree. Extractives are not considered to be structural components of wood. In general, the overall percent of the extractives in wood varies from 2 to 10 percent with the exception of some tropical wood species (20–25%). Extractives are usually divided into three subgroups: aliphatic compounds, terpenes and terpenoids, and phenolic compounds.

According to Stamm and Loughborough (1942) extractives in wood can also be divided into two main classes: 1) extractives deposited in the coarse capillary structure, and 2) extractives deposited in the cell wall structure. Those belonging to class 1 affect the swelling-specific density relationship but do not affect the overall extent of wood swelling. Those belonging to class 2 have a definite influence on the swelling of the cell wall structure and subsequently affect the wood swelling as evidenced by the external dimensional changes.

Stamm and Loughborough (1942) also found that the shrinking and swelling of wood are dependent on the chemical composition, such as water-soluble extractives. The reduction in shrinkage or increase in swelling with removal of extractives is explainable on the basis of mechanical bulking in the cell wall structure with the extractives.

Nayer (1948) found that extracting maple and spruce with neutral solvents appreciably increased the rate of wood swelling in organic liquids. In addition, the final volumetric swelling of wood also dramatically increased in solvents such as pyridine, morpholine, dioxane, and nitrobenzene. Notable was the maximum swelling of extracted spruce in anhydrous benzaldehyde which was more than seven fold as compared to that of unextracted spruce. Nayer concluded that a quicker diffusion and an increased submicroscopic capillary structure were the most plausible explanations for the observed increases in the rate and maximum wood swelling in organic liquids after extraction.

Boiciuc and Petrician (1970) also found that removal of extractives greatly increased shrinkage and swelling of wood. They suggested that the reduction in shrinkage and swelling was proportional to the space occupied by the extractives in the cell walls.

Wangaard and Granados (1967), in their work on the effect of extractives on water-vapor sorption by wood (nine species), found that the increase in fiber saturation point resulting from the removal of extractives was the greatest for a species with a low initial fiber saturation point and the least for a species with a high initial fiber saturation point. The sorption of moisture in polymolecular layers was reduced to a

greatly varying degree, consistent with the theory of bulking action, whereby the extractive substance within the cell wall precluded moisture from occupying the same space.

Mantanis *et al.* (1994a) obtained activation energies for swelling of extracted wood in water. The rate of swelling in water considerably increased after removal of the extractives and the maximum tangential swelling also generally increased on the average by 5–10%. Raising the water temperature above room temperature significantly increased the rate of swelling of extracted wood. It was additionally found that removal of extractives caused a large decrease in the activation energy of wood swelling, E_a (spruce, maple, and aspen).

Material and Methods

Effect of temperature

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 g/cc, and the extractives contents were 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°. They were cut from a single wood stick and the growth rings were parallel to two edges. Care was taken in the selection of wood samples so that any possible variability among the samples (number of annual rings, summer/spring wood, surface characteristics) was diminished. All initial measurements were made at room temperature with a jaw-type vernier caliper, accurate to ±0.05mm and with jaws sufficient to cover the full 25 mm block side of each wood sample. The oven-dry cross-sections were transferred from the oven and cooled in a desiccator. The tangential dimensions were measured as quickly as possible. The average moisture content (MC) was 7–8% on the oven-dry basis. Sitka spruce (*Picea sitchensis*) had an average number of annual rings per cm of 7–8 in the air-dry state. The average specific gravity was 0.38. Sugar maple (*Acer saccharum*) had an average number of annual rings per cm from 5 to 7 in the air-dry state and the specific gravity varied from 0.70 to 0.71; the average was 0.70. Douglas-fir (*Pseudotsuga menziesii*) had an average number of annual rings per cm from 3 to 5 in the air-dry state and the specific gravity was 0.59–0.60. Quaking aspen (*Populus tremuloides*) had 3 to 4 annual rings per cm and the average specific gravity was 0.50. 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.

Anhydrous organic liquids were used in the experiments (with the exception of quinoline (98%), ethylene dichloride (99%), and dibutylamine (99%)). They were stirred in well-sealed bottles over self indicating molecular sieve (sodium aluminosilicate) for two weeks prior to use. The organic liquids selected are representatives of various solvent chemical classes (Table 1). Activation energies of wood swelling were evaluated in all the fifteen liquids. However, due to the time constraint, activation energies of swelling of all four wood species were evaluated for just four organic liquids. In this case, we were able to evaluate the effect of wood species, wood density, and extractives on the temperature dependence of wood swelling. The activation energies of swelling of a representative softwood (spruce) and hardwood (aspen) species were measured with the five different solvent classes to ascertain the

Table 1. Organic liquids selected for determination of wood swelling activation energy

<i>All wood species</i>				
Water	Acetone			
Butylamine	Ethanol			
<i>Sitka spruce and quaking aspen</i>				
<i>Class I</i>	<i>Class II</i>	<i>Class III</i>	<i>Class IV</i>	<i>Class V</i>
High CED ^a	Medium CED	High CED	Low CED	Molar Volume
Low Molar Volume	Low Molar Volume	Low Molar Volume	Low Molar Volume	Greater than 100cc
Hydrogen Bonds	Hydrogen Bonds	No Hydrogen Bonds	No Hydrogen Bonds	
Methanol	Dioxane	Nitromethane	Ethylene dichloride	Toluene
Propanol	Pyridine	Butyrolactone	Carbon tetrachloride	Quinoline Dibutylamine

^a CED: Cohesive Energy Density.

effect of the molecular size, cohesive energy density (CED), dipole moment, and hydrogen bonding parameter on the activation energy (Ea) of wood swelling.

Swelling experiments were carried out in the same apparatus described previously (Mantanis *et al.* 1994a) using a computerized linear variable displacement transformer (LVDT). In a typical experiment, the samples were inserted into the stainless steel swelling apparatus which was immersed in a constant temperature oil bath. The wood sample was placed in a stainless steel holder in the center of the vessel and contacted with the sensor of the LVDT. The preheated swelling liquids were then introduced into the preheated apparatus which was maintained at temperature throughout the experiment. For each liquid, wood swelling rate measurements were made at 3 or 4 temperatures; the upper temperature limit was either the boiling point of the liquid or a temperature close to it. A fresh aliquot of liquid was used at each investigated temperature and the experiment was replicated twice.

Tangential wood swelling was continuously measured with a computer until equilibrium was attained (Figs. 1, 2). Although a very small induction time was usually present, the slope of the initial linear portion of the tangential swelling versus time plot (Fig. 1) was used for the determination of the wood swelling rate (Mantanis *et al.* 1994a, b). Then, from the Arrhenius equation:

$$k = A e^{-E_a/RT} \quad (1)$$

where **k** = swelling rate constant,
A = constant,
R = gas constant,
T = temperature, degrees Kelvin.

plots of $\ln k$ versus $1/T$ gave the activation energies for wood swelling. Ea. Small intervals of time (3 sec–5 min) depending upon the temperature, swelling liquid, and wood species were utilized in order to determine the swelling rate constant k.

Effect of extractives

Heartwood samples of sitka spruce (softwood) and sugar maple (hardwood) were selected for this part of the investigation. These two wood species are representatives of softwoods and hardwoods with different chemical composition, density, and content of extractives. The wood samples were cut and dried as described previously. Only tangential swelling was measured.

We decided to avoid an extraction procedure which would involve a boiling water step. Apparently, boiling water causes significant changes in wood structure and hemicellulosic substances are

removed from the cell wall (Mantanis *et al.* 1994a, b). Thus, wood samples prepared as previously described were extracted with 80% ethyl alcohol for 2 hours. As a result of this mild extraction, sitka spruce lost 3.6% and sugar maple 2.4% of their weights based on the original oven-dry weights. The extracted wood samples were oven-dried for 24 hours at 65°C and then immersed in the various swelling liquids for 100 days. Two cross-sections of unextracted and extracted wood, each of spruce and maple, were swollen in forty organic liquids (Table 2) at room temperature. The maximum tangential swelling of the wood blocks in the anhydrous organic liquids was determined by placing the wood samples in sealed weighing bottles placed in a thermostatically controlled bath (~23°C) for 100 days. The maximum tangential swelling percentage was calculated by the use of the following equation:

$$\text{Percentage swelling} = \frac{(\text{Swollen Dim.} - \text{Oven Dry Dim.})}{(\text{Oven Dry Dimension})} \times 100 \quad (2)$$

The rates of wood swelling in nine organic liquids at room temperature were also evaluated as previously described (Mantanis *et al.* 1994a, b).

Table 2. Categories of liquids selected for wood swelling experiments

Alcohols	Acids	Acetates	Aromatics
Methyl	Formic	Methyl	Toluene
Ethyl	Acetic	Ethyl	Benzaldehyde
Propyl	Propionic	Propyl	Nitrobenzene
Benzyl			
Furfuryl			
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		
Nitromethane	Carbon tetrachloride		
	Ethylene dichloride		

Results and Discussion

Activation energy of wood swelling in organic liquids (E_a)

Maximum swelling values and activation energies for wood swelling in the organic liquids are presented in Table 3. The high R^2 values obtained indicate once again that the temperature dependence of the wood swelling clearly obeys the Arrhenius equation (West 1988; West and Banks 1989). This is also in agreement with findings from our previous work on wood swelling in water (Mantanis *et al.* 1944a). Therefore, these results suggest that the swelling of wood can be viewed as an activated process and furthermore, as a classical chemical reaction. This reaction is featured by the following characteristics:

- (1) The chemical reactants are the wood cell wall and the organic liquid. In the former, the hydroxyl groups are mutually hydrogen bonded together, while in the latter, the solvent molecules are bonded by dipole-dipole interactions.
- (2) In a reaction, a number of these bonds will be broken to form a transition state with the energy required observed as E_a . However, a part of this energy is contributed from the energy required to pull a liquid molecule away from the bulk of the solvent (West 1988).
- (3) In the final stage, the transition state collapses and the liquid molecule is attached to the wood by hydrogen bonds.

In the "zipper" model proposed by West (1988), it was stated that water swollen or green wood is in a stress-free state. It was assumed that dry wood is strained elastically such that when wood-wood hydrogen bonds are broken the wood swells elastically by virtue of the stored elastic strain energy. Also, it was noted that the measured E_a of wood swelling is accounted for by the summation of two energy requirements necessary for the formation of a swelling transition state (T. S.). Thus, the wood swelling activation energy E_a can be divided in two parts:

- (1) The major part of the measured E_a is that required to break a specific number of wood hydrogen bonds in order to form a space sufficient enough for the liquid molecules to occupy.
- (2) A part of the E_a observed is that required to pull a liquid molecule momentarily away from the dipole-dipole influence of the solvent bulk.

An induction period was observed in almost all the swelling profiles (Fig. 1) which varied considerably in length with the wood species, swelling liquid, and temperature. This period was also noted by West (1988) in his study on the swelling of wood in a few organic liquids. The wood swelling induction period is probably related to the time necessary for the

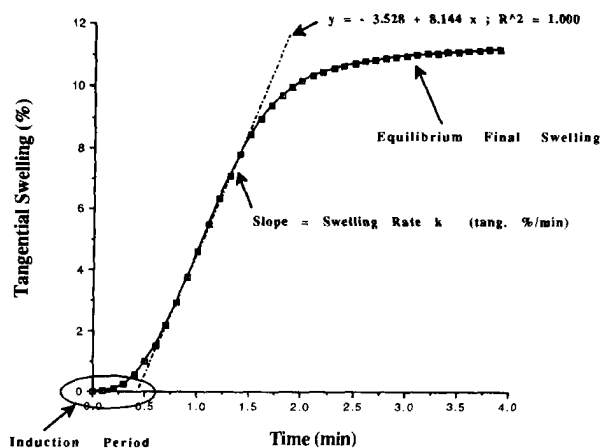


Fig. 1. Schematic swelling profile of aspen in butylamine at 60°C.

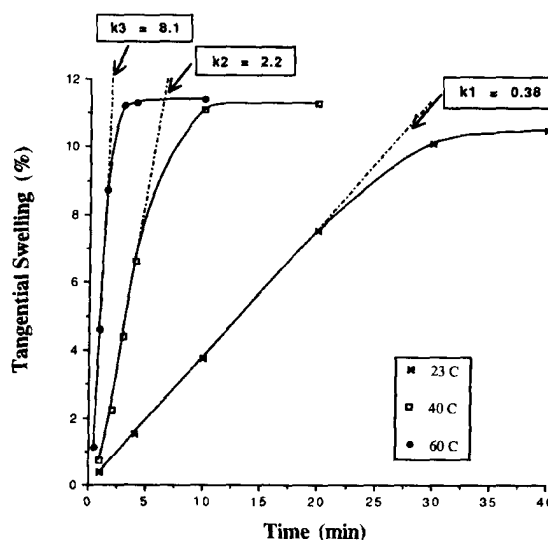


Fig. 2. Swelling of aspen in butylamine at various temperatures.

initial diffusion of the the liquid into the wood cell wall structure. 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 (constant k) (Fig. 1). Similarly Stamm (1956), in his work on the swelling of cellulosic materials, noticed characteristically that after the induction period, the initial 2/3 portion of the tangential swelling profile of spruce in water gave a linear relationship. As shown in Figure 1, the initial portion of the schematic swelling profile of aspen in butylamine at 60°C is

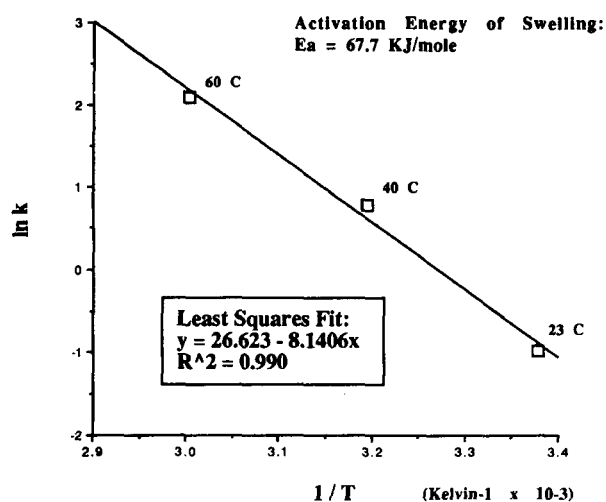


Fig. 3. Arrhenius plot for aspen swelling in butylamine.

linear; the slope of which gives the swelling rate constant ($k = 8.1$ %/min).

Figure 2 shows the three rate constants obtained for the swelling of aspen in butylamine at three different temperatures. It is apparent that the rate of aspen swelling in butylamine increased dramatically from room temperature to 60°C. The time required to reach an equilibrium state decreased drastically from 40 min

(at 23°C) to about 5 min (at 60°C). The activation energy of swelling (E_a) for aspen in butylamine was then calculated from an Arrhenius plot (Fig. 3). In general, the Arrhenius plots showed very strong linear correlations with high R^2 (0.980–1.000) indicating a vigorous dependence of wood swelling on temperature (Table 3).

The rate of wood swelling is mainly affected by both the magnitude of the E_a and the pre-exponent factor A (Eq. 1), that is to say, the size and shape of the swelling liquid, the strength of the wood hydrogen bonds (wood species), and the solvent dipole moments are of significant importance. It is then anticipated that large molecular size solvents should result in a very high E_a of wood swelling. Indeed, the activation energies for wood swelling (KJ/mole; spruce, aspen) in dibutylamine (179, 151), toluene (146, 149), and quinoline (132, 130) were found to be extremely high. This indicates that the solvent molecular size is of very great importance and that, in general, swelling of wood in liquids with large molecular size will be facilitated by elevated temperature. It was indeed found that liquids with large molecular size (quinoline, dibutylamine, toluene, ethylene dichloride and carbon tetrachloride) swelled wood very fast at elevated temperatures (80 to 100°C) and swelling reached an equilibrium state in a period of 5 to 10 minutes, while at room tempera-

Table 3. Maximum tangential swelling values and activation energies (E_a) for wood swelling in various organic liquids

Swelling liquid	S. Spruce			Q. Aspen		
	Maximum ^a Swelling (%)	E_a ^b (KJ/mol)	R^2 ^c	Maximum Swelling (%)	E_a (KJ/mol)	R^2
Water	5.7 (0.3)	32.0	0.985	7.3 (0.3)	44.1	1.000
Methanol	5.5 (0.2)	40.0	0.998	7.1 (0.3)	40.3	1.000
Ethanol	4.7 (0.2)	60.4	0.982	6.3 (0.2)	44.3	0.999
Propanol	4.1 (0.2)	87.0	0.996	5.0 (0.3)	61.8	1.000
Acetone	3.8 (0.3)	56.1	0.984	6.0 (0.3)	49.6	0.997
Pyridine	8.0 (0.3)	93.0	0.995	9.6 (0.3)	59.6	0.999
Dioxane	4.3 (0.3)	95.0	0.992	6.5 (0.2)	68.7	0.998
Nitromethane	2.8 (0.2)	67.1	0.996	4.5 (0.3)	57.4	0.998
Butyrolactone	4.8 (0.2)	88.3	1.000	6.8 (0.3)	65.1	0.998
Ethylenedichloride	1.8 (0.1)	67.9	0.997	3.2 (0.2)	73.4	0.999
Toluene	0.7 (0.2)	145.5	0.976	0.9 (0.2)	149.2	0.974
Carbontetrachloride	0.7 (0.2)	193.7	0.987	0.8 (0.2)	160.7	0.999
Quinoline	1.0 (0.3)	132.1	0.977	1.3 (0.3)	130.1	0.981
Butylamine	9.7 (0.4)	74.6	0.982	12.1 (0.5)	68.1	0.991
Dibutylamine	0.8 (0.2)	179.4	0.975	0.6 (0.2)	150.7	0.969
	Douglas-fir			S. Maple		
Water	6.8 (0.3)	33.1	0.999	8.4 (0.3)	47.7	0.982
Ethanol	5.0 (0.1)	57.1	0.999	7.0 (0.2)	47.4	0.998
Acetone	4.2 (0.3)	29.0	0.995	5.7 (0.2)	54.7	0.977
Butylamine	12.3 (0.4)	36.2	0.997	14.1 (0.3)	66.4	0.993

^a Standard deviations in the parentheses (10 runs each); ^b E_a is the average of two replicates except for water (5 runs); ^c R^2 obtained from the Arrhenius plots ($\ln k$ vs. $1/T$) (average of 2 runs).

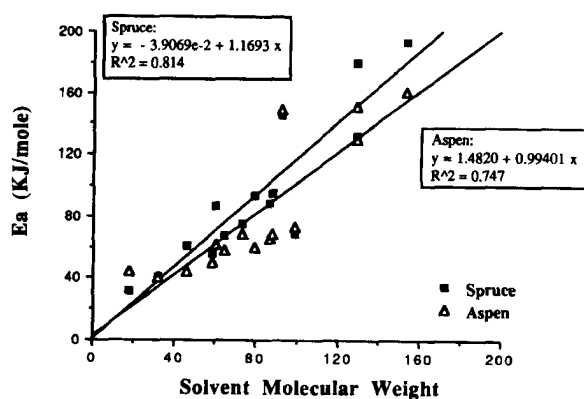


Fig. 4. Activation energy of wood swelling (E_a) versus solvent molecular weight.

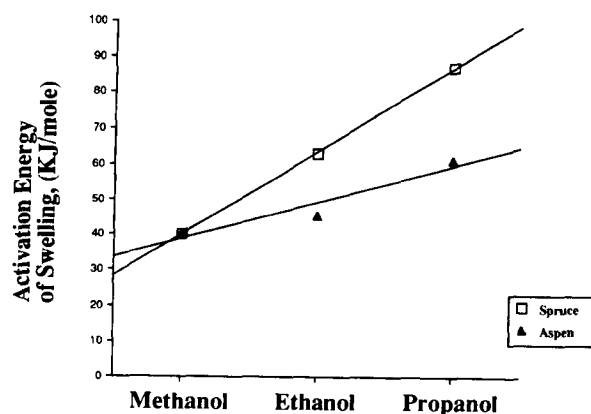


Fig. 6. Activation energies for wood swelling in alcohols.

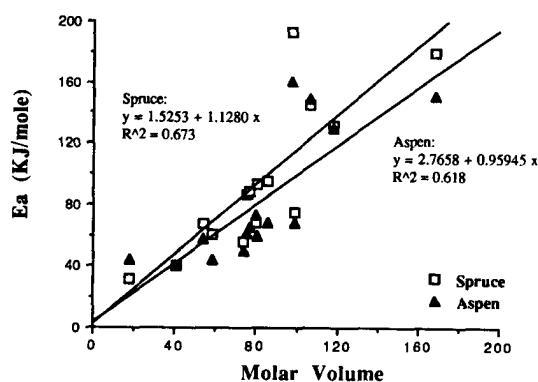


Fig. 5. Activation energy of wood swelling (E_a) versus solvent molar volume.

results were found in the work of West and Banks (1989) on the wood swelling in anhydrous quinoline at elevated temperatures (140- 175°C).

It was also found that a strong linear relationship existed between the E_a of wood swelling and the solvent molecular weight (MW) (Fig. 4). Consistent linear trends were also found to exist between E_a and molar volume (MV) (Fig. 5). Very similar trends were found for the activation energies for wood swelling within a homologous series of alcohols (Fig. 6). It is apparent that, in this case, the addition of a $-CH_3$ group causes a subsequent increase in the E_a . Overall, all these results clearly show that any increase in the molecular size (MW or MV) of the swelling liquid causes a consequent increase in the activation energy of wood swelling. However, as shown by West (1988) with pentanol and quinoline, other factors such as molecular

ture (23°C), it took approximately three months to reach a maximum (Mantanis *et al.* 1994 b). Similar

Table 4. Swelling liquid properties versus E_a of wood swelling

Liquids	HBP*	CED**	E_a (spruce) (KJ/mole)	E_a (aspen) (KJ/mole)
Water	high	high	32.0	44.1
Methanol	high	high	40.0	40.3
Ethanol	high	high	60.4	44.3
Propanol	high	high	87.0	61.8
Pyridine	high	medium	93.0	59.0
Butylamine	high	low	74.6	68.1
Quinoline	high	low	132.1	130.1
Dibutylamine	high	low	179.4	150.7
Acetone	medium	medium	56.1	49.6
Dioxane	medium	medium	95.0	68.7
Butyrolactone	medium	high	88.3	65.1
Nitromethane	low	high	67.1	57.4
Ethylene dichloride	low	low	67.9	73.4
Toluene	low	low	145.5	149.2
Carbon tetrachloride	low	low	193.7	160.7

* Hydrogen bonding parameter (HBP) data from Lieberman (1962); ** Cohesive energy density (CED) data from Robertson (1964).

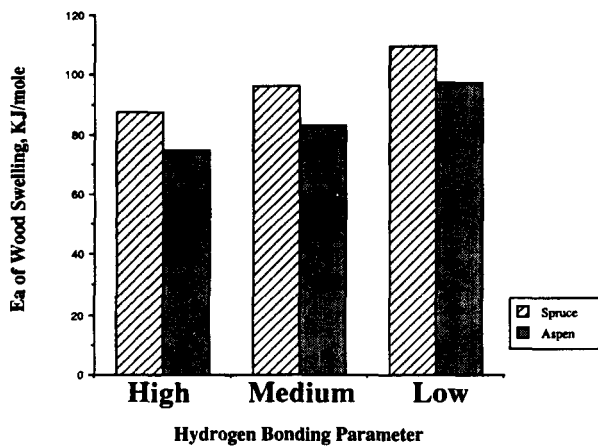


Fig. 7. The effect of the solvent hydrogen bonding parameter on the activation energy of wood swelling.

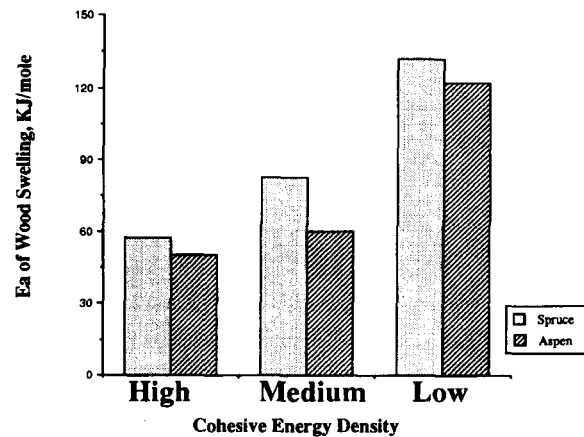


Fig. 8. The effect of the solvent cohesive energy density on the activation energy of wood swelling.

shape or branching, and steric hindrance may also play a significant role. Indeed, by comparison of wood swelling with butylamine (excellent swelling agent) and dibutylamine (poor swelling agent), it can be seen that the steric hindrance and the large molecular size greatly affect the Ea of wood swelling in dibutylamine. Dibutylamine had an Ea of 179 and 151 KJ/mole (for spruce and aspen, respectively) which was more than twice as high as the Ea with butylamine (75 and 68 KJ/mole for spruce and aspen, respectively) (Table 3). It was additionally found that no correlations existed between wood swelling Ea and density of the wood species.

Table 4 shows the Ea of swelling for spruce and aspen wood in relation to the hydrogen bonding parameter (HBP) and the cohesive energy density (CED) of the swelling liquid. In general, solvents

with a medium to low HBP seem to have a higher Ea especially if this accompanied with low CED. Exceptions include quinoline (steric hindrance effect) and dibutylamine (very high molar volume) which exhibited extremely high Ea. Also, as the CED of the liquid decreases (medium to low) the wood swelling Ea increases significantly. On the average, all the low to medium CED solvents such as quinoline, dibutylamine, toluene, carbon tetrachloride, dioxane, pyridine had high Ea. However, butylamine which has a very low CED is the exception in this trend. It is well known (Stamm 1964) that all primary amines (butylamine, ethylamine, etc.) have a very strong swelling action on wood. Both these trends are illustrated in Figures 7 and 8. Each column represents the average Ea in each solvent class (low, medium, and high HBP or CED).

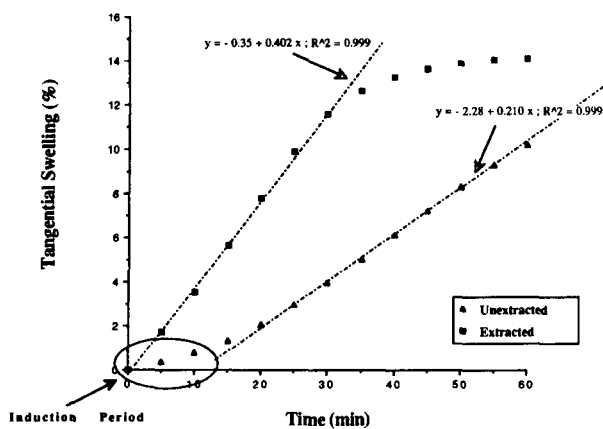


Fig. 9. Initial linear swelling (maple in DMF at 23C). Swelling rate $k = \text{Slope (tang. \% per min)}$.

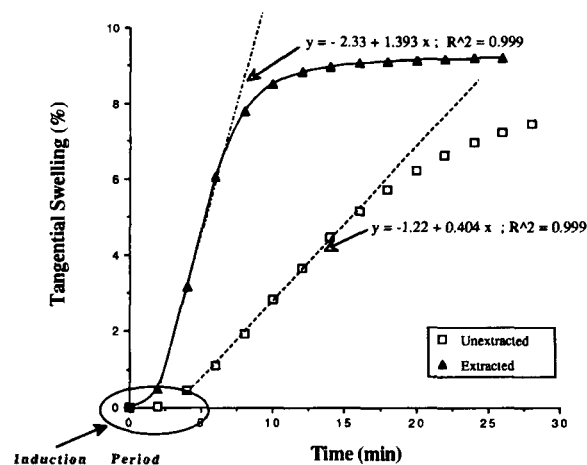


Fig. 10. Swelling of unextracted and extracted spruce wood in butylamine at 23C.

Table 5. Maximum tangential swelling of unextracted and extracted wood in 40 organic liquids

	Sitka Spruce				Sugar Maple			
	Unextracted		Extracted		Unextracted		Extracted	
Water	5.9	(0.3)*	6.3	(0.2)	9.5	(0.3)	10.6	(0.3)
Formamide	8.1	(0.3)	8.0	(0.3)	13.3	(0.3)	13.9	(0.2)
Ethylene glycol	6.9	(0.2)	7.1	(0.3)	10.0	(0.2)	10.8	(0.2)
Methanol	5.8	(0.3)	6.1	(0.2)	9.2	(0.2)	10.2	(0.3)
Ethanol	5.0	(0.2)	5.6	(0.2)	8.2	(0.3)	9.7	(0.3)
Propanol	4.3	(0.2)	4.4	(0.3)	5.6	(0.2)	6.7	(0.2)
DMF	8.0	(0.2)	8.2	(0.4)	12.5	(0.2)	14.4	(0.3)
Pyridine	8.4	(0.2)	8.6	(0.2)	12.3	(0.3)	14.3	(0.3)
Acetone	4.6	(0.2)	4.7	(0.3)	6.4	(0.2)	8.0	(0.2)
2-Butanone	4.2	(0.3)	4.2	(0.3)	5.2	(0.2)	7.0	(0.2)
Dioxane	5.3	(0.3)	6.7	(0.3)	8.3	(0.3)	9.9	(0.3)
Ethylacetate	2.8	(0.3)	3.1	(0.3)	4.0	(0.2)	6.1	(0.3)
Butyraldehyde	0.4	(0.2)	0.6	(0.1)	1.0	(0.1)	2.2	(0.1)
Methylacetate	3.7	(0.3)	4.2	(0.2)	5.2	(0.2)	6.9	(0.1)
Propylacetate	1.1	(0.1)	2.0	(0.2)	2.3	(0.2)	4.6	(0.2)
Nitromethane	2.7	(0.1)	2.8	(0.2)	5.3	(0.2)	6.6	(0.2)
Butyrolactone	5.0	(0.2)	6.5	(0.3)	8.3	(0.3)	10.0	(0.2)
Furfural	4.0	(0.2)	5.7	(0.2)	7.6	(0.2)	9.4	(0.3)
Chloroform	2.6	(0.2)	3.4	(0.2)	4.3	(0.3)	6.4	(0.3)
Ethylene dichloride	2.2	(0.2)	2.1	(0.2)	3.3	(0.2)	4.6	(0.2)
Carbon tetrachloride	1.1	(0.1)	1.5	(0.1)	1.4	(0.1)	1.7	(0.1)
Benzaldehyde	1.6	(0.1)	2.2	(0.1)	1.7	(0.1)	8.5	(0.2)
Nitrobenzene	1.8	(0.1)	1.9	(0.1)	1.7	(0.1)	3.7	(0.2)
Toluene	1.2	(0.2)	1.3	(0.2)	1.5	(0.1)	2.3	(0.1)
Isopropyl ether	1.7	(0.1)	1.9	(0.1)	1.4	(0.1)	1.8	(0.1)
Benzyl alcohol	3.6	(0.2)	6.7	(0.3)	8.3	(0.3)	12.4	(0.4)
Quinoline (98%)	0.22	(0.0)	0.29	(0.0)	0.25	(0.0)	0.30	(0.1)
Octane	1.1	(0.1)	1.2	(0.1)	0.68	(0.0)	0.79	(0.1)
Furfuryl Alc. (99%)	6.7	(0.2)	8.6	(0.3)	10.8	(0.3)	13.3	(0.5)
DMSO	8.6	(0.3)	9.1	(0.3)	15.7	(0.4)	16.0	(0.4)
Benzyl benzoate	1.4	(0.1)	1.5	(0.2)	0.96	(0.1)	1.58	(0.1)
Formic acid (96%)	11.4	(0.3)	12.6	(0.3)	19.3	(0.5)	19.9	(0.5)
Acetic acid	5.6	(0.2)	5.7	(0.2)	9.4	(0.3)	11.4	(0.2)
Propionic acid	4.1	(0.2)	5.3	(0.2)	7.9	(0.3)	9.5	(0.3)
2,6-Dimethylpyridine	1.1	(0.1)	1.9	(0.0)	1.7	(0.1)	10.0	(0.3)
Diethylamine	7.9	(0.3)	8.6	(0.3)	11.1	(0.3)	11.6	(0.2)
Butylamine	11.1	(0.4)	13.3	(0.4)	17.7	(0.5)	19.6	(0.5)
Dibutylamine	0.74	(0.0)	0.80	(0.0)	0.52	(0.1)	0.54	(0.0)
2-Methylpyridine	7.8	(0.3)	10.8	(0.3)	11.6	(0.4)	13.2	(0.3)
Piperidine	1.3	(0.1)	2.3	(0.0)	1.2	(0.1)	10.6	(0.3)

* Standard Deviation.

Effect of extractives on rate and maximum swelling of wood

Table 5 summarizes all the maximum wood swelling results in forty organic liquids. It is notable that the maximum wood swelling increased after the removal of extractives, especially for sugar maple. Also obvious is the very large increase in maximum swelling for maple (benzaldehyde, nitrobenzene, benzyl alcohol, 2,6 dimethylpyridine, and piperidine), and spruce (benzyl alcohol, propyl acetate, 2-methylpyridine, and piperidine) after extraction.

Table 6 shows the wood swelling rate constants obtained for unextracted and extracted wood. It is

clear that a significant increase in the rate of wood swelling took place after removal of extractives (Figs. 9, 10). These increases may be due to the following:

- (1) much quicker diffusion of the swelling liquid into the wood cell wall structure,
- (2) increased chemical reactivity of the swelling liquid towards the various wood polymers that have been freed of extractives,
- (3) possible cell-wall disruption due to the extraction procedure (Mantanis *et al.* 1994, Part I),
- (4) probable increase in the size of the microscopic capillaries during the process of extraction.

Table 6. Swelling rates of unextracted and extracted wood (tangential % per min)

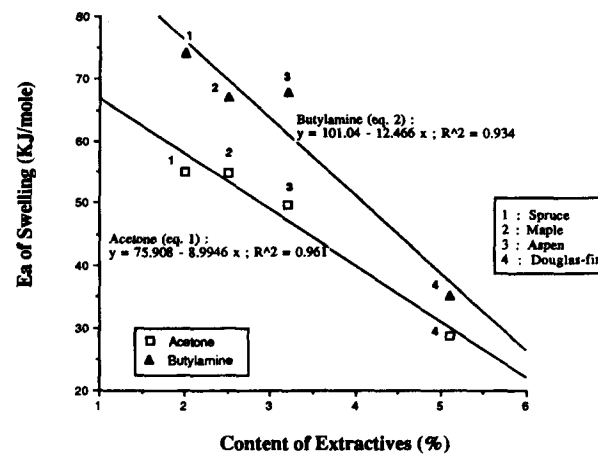
Liquids	Sitka Spruce		Sugar Maple	
	Unextracted	Extracted	Unextracted	Extracted
Methanol	1.980	5.250	1.030	2.100
Formamide	0.034	0.260	0.080	0.099
Acetic acid	0.028	0.048	0.217	0.330
Acetone	4.4 E-4	0.018	0.095	0.500
Butylamine	0.400	1.390	0.432	1.170
Ethanol	0.049	0.180	0.194	0.540
DMF	0.212	0.560	0.210	0.400
DMSO	0.110	0.086	0.055	0.126
Water	1.240	3.170	0.384	0.820

Note: Average of 2 replicates.

Wood extracts were analyzed by high pressure liquid chromatography (HPLC) which showed that a significant quantity of sugars were removed in the extraction procedure (Mantanis *et al.* 1994a). It appears that the sugars are derived primarily from the hemicelluloses in the cell wall; which also implies that the cell wall may have been somewhat disrupted in the extraction process. Thus the whole internal structure of the cell wall was probably disrupted, the network of secondary bonds decreased, and the overall cell wall structure was in a more loosely bonded state. This may explain the large increases in the maximum tangential swelling of wood after removal of extractives.

Figures 9 and 10 illustrate how unextracted and extracted wood swelled differently in the various organic liquids. Generally, in most cases, the swelling of extracted wood was obviously more rapid than that of unextracted wood, and also it reached an equilibrium state in a shorter period of time.

Extractives also seemed to affect the wood swelling E_a . Strong linear correlations existed between the wood swelling E_a and the content of extractives in the wood species as shown for the wood swelling in acetone and butylamine (Fig. 11). West (1988) found an E_a of 48 KJ/mole for the Scots pine swelling in acetone (Scots pine extractives' content is approximately 3.2% (Fengel and Wegener 1984)). This E_a value is in a very good agreement with our results (47 KJ/mole) (Fig. 11; eq. 1). Similar trends were found for the wood swelling in water. However, no correlation was found between E_a and content of extractives in the case of wood swelling in ethanol. Therefore, it is difficult to derive clear conclusions. However, it may be said that, in the case of wood swelling in acetone, butylamine, and water, an increase in the percent of extractives in the wood

**Fig. 11.** Effect of extractives on E_a of wood swelling in acetone and butylamine.

generally caused a decrease in the wood swelling E_a .

Conclusions

The rate of wood swelling in organic liquids is clearly dependent upon the temperature and very closely obeys the classical Arrhenius equation. Thus, the overall wood swelling process can be viewed as a chemical reaction. Some liquids that swell wood only slowly or not at all under room temperature conditions will do so by raising the temperature. Data from the variation of wood swelling rate with temperature were used to derive activation energies (E_a) for the wood swelling process in fifteen various organic liquids. Wood swelling E_a was linearly correlated with the molecular weight and the molar volume of the swelling liquid. Also, extractives adversely influenced the E_a of wood swelling in certain organic solvents, and the swelling of extracted wood took place much faster than that of unextracted wood (spruce and maple). In addition, it was found that removal of extractives from wood caused a significant increase in the maximum tangential swelling of wood.

References

- Ashton, H.E. 1973. The swelling of wood in organic solvents. *Wood Science* 6: 159–166.
- Boiciuc, M., and C. Petrician. 1970. Dimensionsstabilisierung von Rotbuchenholz durch Anlagerung von Styrol. *Holztechnologie* 11(2): 94–96.
- Fengel, D., and G. Wegener. 1984. *Wood: Chemistry, Ultrastructure, Reactions*. Walter de Gruyter, Berlin, New York.
- Ishimaru, Y., and H. Sakai. 1988. Swelling of wood in liquid mixtures. *Mokuzai Gakk.* 34: 889.
- Kumar, B.V. 1957. Swelling studies in wood. *Norsk Skogind.* 57(7): 259–268.
- Kumar, B.V. 1958. Swelling studies in wood. *Norsk Skogind.* 58(9): 337–345.

- Lieberman, E.P. 1962. Quantification of the hydrogen bonding parameter. *Official Digest*, January, 30–50.
- Mantanis, G.I., R.A. Young, and R.M. Rowell. 1994a. Swelling of wood. Part I. Swelling in water. *Wood Sci. Technol.* 28: 119–134.
- Mantanis, G.I., R.A. Young, and R.M. Rowell. 1994b. Swelling of wood. Part II. Swelling in organic liquids. *Holzforschung* 48(6): 480–490.
- Nayer, A.N. 1948. Swelling of wood in various organic liquids. Ph.D. Thesis. University of Minnesota, Minneapolis.
- Robertson, A.A. 1964. Cellulose-liquid interactions. *Pulp and Paper Mag. Canada* 65: 171–178.
- Rowell, R.M., and W.D. Ellis. 1984. Reaction of Epoxides with Wood. *Advances in chem. ser.* 207. Amer. Chem. Society, Washington.
- Saechting, V., and H. Zocher. 1934. Die Volumenquellung von Fichtenholz und von Lignin in verschiedenen Flüssigkeiten. *Kolloid Beihefte* 40: 413.
- Stamm, A.J. 1935. Shrinking and swelling of wood. *Ind. Eng. Chem.* 27: 401–406.
- Stamm, A.J., and W.K. Loughborough. 1942. Variation in shrinking and swelling of wood. *Trans. Amer. Soc. Mech. Eng.* 64: 379–386.
- Stamm, A.J. 1956. Diffusion in cellulosic materials. *Australian Pulp and Paper Industry Technical Association Proceedings* 10: 244–270.
- Wangaard, F., and L. Granados. 1967. The effect of extractives on water-vapor sorption by wood. *Wood Sci. Technol.* 1: 253–277.
- West, H. 1988. Kinetics and mechanism of wood-isocyanate reactions. Ph.D. Thesis. University of North Wales, Bangor, Great Britain.
- West, H., and W.B. Banks. 1989. A chemical kinetics approach to the process of wood swelling. In: *Proc. Tenth Cellulose Conf. Ed. C. Schuerch.* p. 1215. John Wiley & Sons, New York

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