SWELLING OF LIGNOCELLULOSIC MATERIALS IN WATER AND ORGANIC LIQUIDS

by

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Abstract

The rate and maximum swelling of several North American wood species in water and in various organic liquids have been investigated in this work with a computer interfaced linear variable displacement transformer (LVDT). The strict linear dependence of wood swelling on the temperature clearly suggests a chemical mechanism. Activation energies, E_a, for wood swelling in water, obtained from Arrhenius plots, ranged from 32.2 KJ/m for spruce to 47.6 KJ/m for maple. It was found that many similarities existed between wood and cellulose maximum swelling behavior within various solvent chemical classes. It is suggested therefore that cellulose is primarily responsible for the major amount of wood swelling. In general, all swelling liquids having a molar volume greater than 100 cc or a low hydrogen bonding capability, caused very little wood swelling. The logarithm of the swelling rate of wood in liquids was inversely correlated with the solvent molecular size. The maximum tangential swelling was linearly correlated with the solvent basicity (donor number). Thus, the swelling of wood in organic solvents is mainly influenced by three solvent properties, solvent basicity, molar volume and hydrogen bonding capability. Wood wetting experiments showed that wood surfaces have a strong acidic character since the greatest interactions for all the wood species tested occurred with formamide (basic probe), while lesser interactions occurred with ethylene glycol (acidic probe). The total surface free energy of wood ranged from 48.0 to 61.0 dyn/cm, on the average, with 75 to 80 % of this energy attributed to dispersion forces. No correlation existed between wood specific wettability and maximum tangential swelling of wood in various liquids. Hydrogen bonding capability, molecular size, and cohesive energy density of the swelling liquid appeared to be the most important parameters in the swelling of various cellulosic fibers in organic liquids (compressed fiber systems). Correlations between cellulose compressed fiber pellets and wood swelling in the various liquids were generally quite good.

Approved by Raymond A. Young
Professor of Wood Chemistry

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CHAPTER ONE

INTRODUCTION

An important property of wood from the standpoint of structural use is swelling. The artificial minimization of wood swelling for structural purposes is important for wood to retain present markets and to increase in use. The phenomenon of swelling is characteristic of all elastic materials but differs somewhat for different types of materials. In general, a solid is said to swell when it takes up a liquid and at the same time fulfills the following three 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 a microscopic sense, (c) Its cohesion is diminished but not eliminated, that is, it becomes soft and flexible instead of hard and brittle. Cellulosic materials show a precisely oriented structure that results in differences in the dimensional swelling in the three structural directions. It is characteristic that cellulosic materials differ from other materials (i.e. gelatin) still further in that they show a coarse capillary structure that is able to take up liquids without accompanying swelling, as well as the characteristic capillary influence on swelling. This therefore makes the measurement of the swelling of cellulosic materials even more complicated. So-called swelling measurements have been made on cellulosic materials by evaluating the increase in weight of the material after immersion in various organic and inorganic liquids and solutions. This gives a measure of the absorbency and depends on the capillary structure of the material, the surface tension of the liquid, and the ability of the liquid to wet the solid as well as on its swellability (extent of swelling) (Stamm, 1934). In wood, the external dimensional changes are easy to determine but the internal changes in the fiber cavities are not as clearly ascertained; only approximations of these changes can be made. A study of these dimensional changes, however, is beneficial because it will lead to a better understanding of the mechanism of the swelling of wood and cellulosic materials in liquids.

The swelling of wood as manifested by the external dimensional changes varies with the species, structure, density, drying conditions, etc. The fiber saturation point (FSP) of wood is also a significant factor. This point varies for most wood species from 27 to 32 percent of the weight of the dry wood (Stamm, 1929; Stamm, 1964). Usually species with a high percentage of extractives have a relatively lower fiber saturation points. The swelling is greatest in the tangential direction (tangent to the annual rings) varying usually from 5 - 12 %. In the radial direction (from the center of the tree to the periphery) it varies from 50 - 70 % of that of the tangential swelling, and in the longitudinal direction (parallel to the fibers) it is almost minimal. The practically negligible longitudinal wood swelling is accounted for by the almost parallel orientation of the length of the fibers in the longitudinal direction of wood. The greater swelling in the tangential direction than in the radial is due to the greater amount of total wood substance in the tangential direction and also to the fact that ray cells, which extend radially in a tree, tend to restrain dimension changes in the radial direction (Stamm, 1964).

The swelling of wood with liquids is also 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. The swelling of wood in water and in an extensive series of organic solvents has been investigated in this doctorate thesis. Since organic liquids are the basis of many reactions and modifications of wood it is important to better understand the interactions of the liquids with the wood to better predict the effects. These results will also be helpful for new developments in solvent pulping (organosolv pulping) of wood.

CHAPTER TWO

LITERATURE REVIEW

2.1. Swelling of Wood in Water and Organic Liquids

The swelling of wood in both liquid water and water vapor has been studied extensively for the past fifty years. A number of scientists have made attempts to determine the factors that influence wood swelling in liquid water and organic solvents. The most extensive work on swelling of wood in liquid water was carried out by Stamm and coworkers (1964). They found a definite correlation of shrinking and swelling of wood with specific gravity and demonstrated this can be predicted by the following qualitative relationship:

$$S = f\,g \qquad 2.1$$

where S is the total volumetric shrinkage from green to the oven-dry condition on a percentage basis, f is the fiber-saturation point on a percentage volume per unit weight basis, and g is the specific gravity of the wood on a swollen volume basis.

Stamm and coworkers (Stamm, 1935; Stamm, 1964; Stamm and Tarkow, 1950) also 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.

Nayer and coworkers (Nayer, 1948; Nayer and Hossfeld, 1949) 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.

Hossfeld (1972) concluded that there is direct relationship between the degree of swelling of wood and its permeability to a liquid. His results for a dioxane-water and an isopropyl alcohol-water system illustrated a direct and uncomplicated relation, that is, the tangential swelling of wood increased with an increase in the permeability. He also found a maximum for the permeability and swelling of the wood, for the binary system dioxane-water, in the range of 0.70 - 0.80 mole fraction of water.

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 for birchwood. The presence of water has been found to significantly influence the swelling of wood in many organic solvents.

Saechtling and Zocher (1934) extended the work of Hasseblatt (1926) 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 dimethylformamide (DMF) swelled wood more rapidly. To swell wood effectively with DMSO required a vacuum impregnation process.

Ma et al. (1991) explored the empirical correlations between the mechanical properties of solvent-treated wood and solvent parameters. Wood beams of birch and Douglas-fir were soaked in five solvents (benzene, dioxane, methanol, DMSO, and water) for four months at 23° C. Acoustic emission (AE), modulus of rupture (MOR), and modulus of elasticity (MOE) of the specimens were correlated with the solvent strength parameter through acceptor number (AN), donor number (DN), and molar volume (MV). A linear correlation of the AE energy of the specimens with the solvent parameter $(AN + DN)^{1/2}$ was verified. All these observations reflect the changes in mechanical properties and microstructure of wood that take place throughout the process of wood swelling.

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.

Ishimaru and Sakai (1988) explained the enhanced swelling of wood in binary liquid mixtures from the standpoint of the activity of each constituent, that is, a positive deviation of the activity of a constituent from the ideal solution means the molecules have a higher secedeability from the cohesion force in the mixture compared to the pure liquid. Thus, the constituent has a greater chance to attack adsorption sites responsible for the swelling of wood than that expected in pure concentration (water-ethanol and water-acetone system).

Morgan and Orsler (1969) found that dioxane ultimately behaved as a swelling solvent for beech with a rate much slower (measured in terms of the tangential dimension changes to reach half the final equilibrium swelling) than that of water. Swelling by water was virtually instantaneous, whilst in dioxane the percentage tangential swelling reached only half of its equilibrium value in two days and reached the final value in excess of seven days. They showed that swelling rate increased progressively as the amount of water in dioxane-water mixtures was increased. They also noticed that there was no direct relationship between swelling rate and volumetric swelling values.

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 et al. (1959) also previously demonstrated a reasonably good correlation between swelling of wood and the W values of various organic solvents.

2.2. Effect of Temperature on Wood Swelling

Rowell and Ellis (Rowell, 1984; 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 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) 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. 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 liquid water and organic liquids (associated) such as pyridine into wood structure to cause swelling. However, application of their technique with liquid water proved very difficult because of the very rapid swelling in water even at room temperature.

2.3. Effect of Extractives on Wood Swelling

Stamm and Loughborough (1942) 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.

Wood samples high in water-soluble extractives were found to invariably shrink less than predicted by Eq. 2.1 (Stamm, 1964). This is due to the bulking effect of the extractives which are left deposited in the cell walls. For example, unextracted redwood has a low apparent f value of about 18; but after extraction with water it rises to 25, which is almost the normal value (Stamm, 1964). Other species high in extractives such as eastern red cedar, juniper, and yew also showed this anomalous behavior due to 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.

2.4. Wettability of Wood

Freeman (1959) measured wood wettability, as defined by the cosine of the advancing angle of water with wood using the inclined plate method (Adam 1938). The plate of wood used to read the angle was a representative shear-block half that had been resurfaced on a jointer shortly before the wettability determination. Relating his results to wood adhesion, he concluded that wettability, pH, and specific gravity are closely related to glue-bond quality. Specific gravity was generally more important, and pH and wettability less, with resorcinol-phenol bonds compared with urea-formaldehyde bonds (with wood).

Gray (1962) in his investigation on wood wettability measured advancing and receding contact angles of water with various different timber species. He introduced a technique for measuring surface tension of solids and for calculating the free energy of wetting, F_W, and the work of adhesion, W_A, for any liquid. It was also shown that surface contamination occurs rapidly on freshly cleaned surfaces.

Herczeg (1965), in his work on the wettability of Douglas-fir wood, found that the critical surface tensions, γ_c, were between 44 to 50 dynes/cm for summerwood and springwood, respectively. The surface-free energy of Douglas-fir, γ_s, was estimated to be around 60 dynes/cm, slightly higher by about 10 dynes/cm than γ_c. Also, the maximum work of adhesion, $W_{A\ max}$, varied from 116.4 to 122.5 dynes/cm. Aging up to 45 hours increased contant angles, θ, from 40.8 to 77.2 degrees, showing that wood wettability was reduced.

Chen (1970) in his work on the effect of extractives on adhesion and wettability of wood found that extractive removal improved wettability and increased the pH of the wood in all the species (tropical) tested. Wettability was obtained for each wood sample by measuring advancing contact angle, θ_A, with distilled water (inclined plate method). Also, a positive linear correlation was found to exist between wettability and joint strength of blocks glued with urea-formaldehyde resin, however, no such correlation existed for blocks glued with resorcinol-phenol resin.

Hse (1972) measured the wettability of southern pine veneers by measuring the contact angles formed with 36 phenol-formaldehyde resins. The contact angle was found not to be correlated with the solids content of the resins. The contact angle of resins on earlywood was less than that on latewood, apparently because earlywood surfaces were rougher. Also, the contact angle was positively correlated with the glue bond quality as tested by wet shear strength, percent of wood failure, and percent of delamination. The results showed that interactions between the physico-chemical characteristics of resin and the properties of the wood substrate may strongly affect bond quality.

Kajita and Skaar (1992) evaluated the wettabilities of the surfaces of some American softwoods species (using cosine θ as the index of wettability). The freshly shaved surfaces wet more easily than the original unshaved rotary veneer surfaces. Also, the earlywood wet more easily than did the latewood (earlywood has a greater roughness factor and a greater porosity). The wetting angles varied from 68 degrees (eastern red cedar) to 14 degrees (Alaska-cedar). The greater wettability of sapwood compared with heartwood was attributed to the extractive content of the heartwood.

Young (1976), in his work on the wettability of wood pulp fibers, demonstrated the applicability of the Wilhelmy technique for measuring wetting properties of a series of wood pulp fibers (unbleached kraft, neutral sulfite semichemical, thermomechanical). Unbleached neutral sulfite semichemical fibers exhibited much greater wettability when compared with thermomechanical pulp fibers which in turn were somewhat more wettable than unbleached kraft pulp fibers. These differences were related to variances in the nature and extent of lignin removal, the presence of hemicelluloses or other carbohydrate material, and extractives at the fiber surface. Also, morphological characteristics of the fiber surface were considered to be important. Grafting of the pulps with styrene greatly reduced the fiber wetting properties.

Hodgson and Berg (1988) also used the Wilhelmy technique to measure dynamic wetting properties of single wood pulp fibers. It was concluded that, for complex material surfaces like those of wood pulp fibers, a wettability profile is very useful in understanding fiber structure and chemistry. Highly bleached, low-lignin content fibers were more hydrophilic than high yield, high lignin content fibers, such as thermomechanical pulp fibers. The presence of residual extractives seemed to have a substantial effect on fiber wettability, especially for pulp subjected to elevated temperatures. Also, the cosine of the single-fiber advancing contact angle was found to be inversely proportional to the absorption time (wood pulp fibers).

Jacob and Berg (1993) used the technique of contact angle titration to demonstrate the change in wetting behavior of four pulp fiber furnishes with varying pH (buffer solution). The changes in wetting were indicative of dissociation or reassociation of ionizable functional groups on the fiber surface and fiber-liquid interfacial free energy. The results were expressed in terms of the acid-base contribution to the work of adhesion, which simply indicates the extent of the specific chemical interactions across the fiber-buffer solution interface. Softwood bleached kraft (SWBK), hardwood bleached kraft (HWBK), and alpha-cellulose fibers had both acidic and basic functional groups, but SWBK and HWBK fibers were slightly more acidic and α-cellulose fibers were slightly more basic. Chemithermomechanical (CTMP) fibers did not have as evenly balanced acid and base sites as the other three fiber types, but were instead mainly acidic. Fernandez (1993) also measured wetting of pulp fibers (sulfite, kraft, and acetic acid) and concluded that the acid-base work of adhesion of different pulps were higher with the basic liquid probe (formamide) than with the acidic liquid probe (ethylene glycol), thus indicating the strong acidic character of pulp fibers.

Luner and Sandell (1969) evaluated the wetting properties of cellulose and wood hemicelluloses by Zisman's empirical parameter (1964), the critical surface tension of wetting, γ_c. It was found that the source of cellulose (cotton, wood and hydrolyzed cellulose), the method of film preparation (single-bath, two-bath, dry-cast, orientation), and also the physical state of the cellulose surface influenced the wettability of the samples. The critical surface tension ranged from 35.5 to 49.0 erg cm^{-2} for cellulose and from 33.0 to 36.5 erg cm^{-2} for hemicellulose films. The hemicellulose samples showed the smallest hysteresis effects presumably due to the energetically more uniform surface and lower porosity. It was also concluded that the interaction of cellulose with liquids ranging from water to non-polar liquids involved, in addition to hydrogen bonding, strong dispersion forces.

Lee and Luner (1972) measured the wetting and interfacial properties of six different lignin preparations. No significant differences were found in their wetting characteristics (contact angle, critical surface tension). These similarities were considered as a result of the hydrophilic and amorphous nature of lignin. As with hemicellulose, and to some extent cellulose, monolayers of water were sufficient to equalize the surface energy of the lignins so that the surface was essentially water-like.

It was additionally concluded that when a liquid interacts with lignin or cellulose, even when dry, the non-dispersion forces contribute greatly to the total energy.

2.5. Swelling of Cellulose and Lignin in Water and Organic Liquids

Only limited data are available for the cross-sectional swelling of cellulose fibers because of the time consumed in making a single accurate measurement and the need to measure a large number of fibers to obtain a reasonable average. Reported values of the percent swelling, corrected for lumen area, ranged from 31 - 33 % for cotton of different varieties and maturity and 65 % for viscose rayon fibers (Stamm, 1964; Moore et al., 1950; Welo et al., 1952). These results are much lower than those for swelling of cellophane which swelled 137 % in volume in water. Essentially all of the water that enters the voids in the cellophane results in swelling in this case (Stamm, 1964; Stamm, 1956).

Another method for determination of swelling of cellulose fibers is by measurement of the centrifugal water retention value (Hopner et al., 1955). This empirical method is frequently used because of simplicity, but it gives values which are very low for highly swollen pulps (Scallan and Carles, 1972). The solute exclusion technique, introduced by Aggebrandt and Samuelsen (1964), has been the most widely utilized method in recent years. Stone et al. (Stone and Scallan, 1967; Stone et al., 1969; Scallan, 1977) applied the technique to determine the fiber saturation point of wood pulps using sugars and dextrans as the porous probe molecules. By measuring concentration changes for a series of solutions comprised of molecules of different sizes, they were able to determine the amount of accessible and inaccessible water. They found a wide range of swelling for both rayon and cellophane samples with textile rayon swelling to a greater extent than tire cord rayon, but both much less than cellophane (Stone et al., 1969). Sulfite wood pulps were found to swell to a greater extent than kraft pulps. However, it is important to note that the large increases in the amount of water within the cell wall that accompanies pulping is not necessarily followed by a concomitant increase in swelling (Scallan, 1977).

Robertson (1964) carried out an investigation on cellulose-liquid interactions and based his swelling interpretations on accessibility measurements of the cellulose using a technique of solvent exchange with thallous ethylate in benzene. He evaluated the effects of molar volume, solubility parameter and liquid dipole interactions on swelling of cellulose fibers. He concluded that molar volume is important to swelling. None of the experimental liquids having a molar volume greater than 100 cc increased the swelling of cellulose to any appreciable extent, even though, some of the liquids are capable of strong hydrogen bonding. Liquids which are strongly associated with the Bottcher (1952) or Pauling (1950) criterion (dipole interactions) do not increase the swelling of cellulose fibers appreciably if they are not capable of participating in hydrogen bonding. He found that hydrogen bonding liquids which are not associated (proton acceptors which do not have proton donor properties) form a second series of correlations in which the fiber swelling is correlated with cohesive energy density (solubility parameter). The remaining non-associated, non-hydrogen bonding liquids did not swell cellulose appreciably. Robertson noted with fibers, as did Nayer and Hossfeld (1949) with wood, that some binary mixtures of liquids can produce more swelling than either component alone. This synergistic effect is particularly notable when water is one of the liquids. In another publication, Robertson (1970) suggested that the factors that determine the effectiveness of the immersion liquid in cellulose include the hydrogen bonding properties and the existence of intermolecular forces that are summed up in the cohesive energy density. In addition, other factors such as molecular volume and steric effects are also of importance. The interaction with cellulose fibers depends additionally on the structure and porosity of the fiber.

Chitumbo and Brown (1974) in their experiments on the temperature dependence of swelling of homogeneous cellulosic gels found that temperature had a significant influence on the swelling of cellulose gels. They used a thermostated cylindrical cell and followed progress by measuring the column height with a cathetometer. Particularly notable was the dramatic effect of temperature on the swelling of cellulose gels in dimethylsulfoxide (DMSO).

Thode and Guide (1959), by application of the Hildebrand solubility parameter, presented a hypothesis to explain the swelling behavior of cellulose in organic liquids. They concluded that the apparent total surface (mostly internal) was a function of the swelling produced by the solvent. It was also noted that the greater the cohesive energy density of the liquid, the greater the ability of the retreating solvent layer to pull elements of the polymer structure together. They also found that a linear relationship existed between the volume increase swelling of cellulose fibers in various polar liquids and the solvent solubility parameter (δ). Amines characteristically did not follow this correlation. It is well known that these particular liquids can penetrate even the highly ordered crystalline regions of a cellulosic fiber (Stamm and Tarkow, 1950; Thode and Guide, 1959).

Philipp et al. (1973), in their work on the swelling of cellulose in organic liquids, found that no correlations whatsoever existed between maximum liquid retention value (LRV) and individual solvent properties such as dielectric constant, dipole moment, and cohesive energy density. However, three other parameters were found to be of importance to cellulose swelling in organic liquids: (a) the hydrogen bonding fraction δ_H and the polar fraction δ_P of the CED, (b) the solvent molar volume, and (c) the cellulose structure especially the width and distribution of voids, and the lateral-order spectrum. It was also observed that a high δ_H and δ_P synergetically increased swelling. A high molar volume was not detrimental to swelling if connected with a high δ_H, and if a large enough void structure permitted the penetration of the liquid into the fibrous sample. The final LRV was found to be dependent mainly upon the interrelation between molar volume of the swelling agent and the void structure of the fiber sample.

Steiger and Kapur (1972), in their work on the liquid absorption by compressed cotton fibers, found that the weight capacity of various compressed fiber systems was a linear decreasing function of increasing bulk density. On the other hand, the volume capacity versus bulk density relationships were curves with a peak; each environmental pressure produced an optimum volume capacity in the region of a bulk density of about 0.8 g/cm^3. It was also observed that below a bulk density of about 0.2 g/cm^3, contact with liquid caused a reduction in the total volume of the absorbent (i.e. cotton, rayon).

Kress and Bialkowsky (1931) measured rates and maximum swelling values of cellulose fibers in various pure organic liquids at room temperature using a mercury dilatometer (expansion of mercury). The swelling was given as the volume percent increase of the compressed pulp fibers (density ~ 1.00 g/cc). The rate of swelling was generally very rapid and the maximum swelling was attained in a few hours. The swelling power of water was quite high (90 %), while the swelling power of fuel oil was extremely low (2 %). Formamide had an extremely high swelling power (125 %). The swelling power of ethylene glycol (89 %) was practically the same as that of water. The swelling power of the alcohols (methyl, ethyl, propyl, butyl, amyl) decreased as the length of the hydrocarbon chain increased. The increase in pulp volume with methanol was 62 %, with ethanol was 40 %, and with the higher alcohols was extremely low (4 - 6 %). The pulp swelling in furfural was also very low (8 %). Using a similar but modified dilatometer, Mckenzie (1956) also measured the swelling capacity of cellulose pulps in various liquids. He concluded that liquids which produce a significant amount of swelling are those which are capable of forming hydrogen-bonded complexes with the cellulose molecule.

Stamm and Tarkow (1950) found that fibers of cellulose and lignocellulosic materials such as wood can be directly penetrated only by polar liquids. The extent to which a liquid will penetrate fibers and swell them appears to be dependent upon the ability of the swelling liquid to form hydrogen bonds with the hydroxyl groups of cellulose or lignin, and also upon the size of the liquid molecules.

CHAPTER THREE

OBJECTIVES

The research objectives in this investigation are as follows:

(1) To determine the mechanisms of wood swelling in water and organic liquids.

(2) To investigate the relative importance of liquid and substrate properties on the swelling of wood in organic liquids.

(3) To evaluate the role of wood polymers in wood and fiber swelling.

(4) To determine the effect of temperature on the swelling of wood in water and various organic liquids.

(5) To evaluate the wetting properties of wood in relation to wood swelling.

CHAPTER FOUR

EXPERIMENTAL

4.1. Materials

4.1.1. Wood Swelling in Water

Distilled water was used in the swelling experiments. Heartwood samples of sitka spruce, Douglas-fir, sugar maple and quaking aspen were selected for the investigation. The samples were cut in the form of 25 (tangential) x 25 (radial) x 5 (longitudinal) mm pieces and oven-dried for 24 hours at 65° C.

Sitka spruce (*Picea sitchensis*) 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*) had an average number of annual rings per cm from 5 to 10 in the air-dry state and the specific gravity varied from 0.66 to 0.72; the average was 0.68. Douglas-fir (*Pseudotsuga menziensii*) 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 rings/cm and another (Douglas-fir II) for wood samples having higher densities (0.56 to 0.61) with 10 rings/cm; quaking aspen (*Populus tremuloides*) had 12 annual rings per cm and the average specific gravity was 0.48.

Only tangential swelling was measured. The longitudinal direction was chosen to be the shortest one (5 mm) to accomplish complete penetration of water in a short time.

4.1.2. Wood Swelling in Organic Liquids

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 4-1). These organic liquids have different properties (hydrogen bonding parameter, molar volume, cohesive energy density, basicity, dipole moment, dielectric constant, solubility 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.

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) x 25 (radial) x 5 (longitudinal) mm pieces and dried for 48 hours at 65°C. Their average moisture content (MC) was 6-7 %. Sitka spruce 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 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 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 (0.57-0.60) with 7 to 8 rings/cm; quaking aspen had 6 to 8 annual rings per cm and the average specific gravity was 0.51. Only tangential swelling was measured.

TABLE 4-1

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	
Nitromethane	Carbon tetrachloride	
Pyrrole	Ethylene dichloride	

4.1.3. Wood Swelling at Elevated Temperatures

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 same form as previously described (Chapter 4.1.1) and dried for 48 hours at 65°C. 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 ± 0.05 mm and with jaws sufficient to cover the full 25 mm block side of each wood sample. The dry samples 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 %. Sitka spruce 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 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 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 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 these 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 4-2). 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 effect of the molecular size, hydrogen bonding parameter, cohesive energy density, dipole moment, etc. on the activation energy (E_a) of wood swelling.

4.1.4. Swelling of Extracted Wood in Water and Organic Liquids

Cross-sections of all wood species prepared as previously described (Chapter 4.1.1) were extracted (see Chapter 4.2.3) and swollen in water at five different temperatures (23, 40, 60, 80, and 100°C). Also, sitka spruce (softwood) and sugar maple (hardwood), same as those described previously (Chapter 4.1.3), were extracted and swollen in forty various organic liquids (Table 4-1) for a period of 100 days at room temperature. Only tangential swelling of extracted wood was measured.

4.1.5. Wetting of Wood

Anhydrous organic liquids were used in this study. The test liquids and their surface tensions are shown in Tables 4-3 and 4-4. Surface tensions of the probe liquids were experimentally determined with a small clean glass plate. The measured values were in good agreement with the literature values and the literature values were used

TABLE 4-2

Organic Liquids Selected for Determination of Wood Swelling Activation Energy

All Wood Species

Water	Acetone
Butylamine	Ethanol

Sitka Spruce and Quaking Aspen

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 100 cc
Methanol	Dioxane	Nitromethane	Ethylene dichloride	Toluene
Propanol	Pyridine	Butyrolactone	Carbon tetrachloride	Quinoline
				Dibutylamine

[a] CED: Cohesive Energy Density

TABLE 4-3

Surface Tensions of Organic Liquids [a]

Liquid	Surface Tension (dynes/cm)	Probes
Water	73.00	bifunctional
Formamide	58.30	basic
Ethylene glycol	48.30	acidic
Methanol	22.61	
Ethanol	22.75	
Propanol	23.78	
Dimethylformamide	36.80	
Pyridine	38.00	
Acetone	23.70	
Methylethyl ketone	24.60	
Methylacetate	24.60	
Ethylacetate	23.90	
Propylacetate	24.30	
Nitromethane	36.80	
Furfural	43.50	
Chloroform	27.14	
Ethylene dichloride	23.40	
Carbon tetrachloride	26.95	
Benzaldehyde	40.04	
Nitrobenzene	43.90	
Toluene	28.50	
Benzyl alcohol	39.00	
Quinoline (98%) [b]	50.30	
Dimethylsulfoxide	43.50	
Formic acid (96%) [b]	47.60	
Acetic acid	27.80	
Propionic acid	26.70	
Diethylamine	16.40	
Butylamine	19.70	
Diiodomethane	50.80	neutral
Hexadecane	28.00	neutral

[a] Handbook of Chemistry and Physics (1993)

[b] Surface tensions measured experimentally

TABLE 4-4

Dispersion and Acid-Base Interaction Components of the Surface Tensions of the Probe Liquids

Liquid	γ_L (dynes/cm)	γ_L^{lw} (dynes/cm)	γ_L^{ab} (dynes/cm)
Hexadecane	28.0	28.0	0.0
Ethylene glycol	48.3	29.3	19.0
Diiodomethane	50.8	49.5	1.3
Formamide	58.3	32.3	26.0
Water	73.0	21.6	51.4

Note: γ_L^{lw} : Dispersion component (Lifshitz-van der Waals)
γ_L^{ab} : Acid-base interaction component

in the calculations (Fernandez, 1993; Handbook of Chemistry and Physics, 1993). Heartwood samples of the softwoods, sitka spruce (*Picea sitchensis*) and Douglas-fir (*Pseudotsuga menziensii*), and the hardwoods, sugar maple (*Acer saccharum*) and quaking aspen (*Populus tremuloides*), were selected for this investigation. These wood species were selected as representatives of softwoods and hardwoods with different chemical compositions and specific gravities. Small square wood samples were cut from a fresh log and sawn into 3 mm thick boards. These boards were then cut into specimens 3 mm thick x 3 mm wide x 35 mm long. The specimen surface represented a flatsawn or tangential surface. Gray (1962) reported that there was no difference between radial and tangential wettability for wood surfaces; therefore, differences in grain orientation were not evaluated in this work. Wood samples were then dried in oven for 24 hours (65° C). After drying, a small quantity of epoxy was placed on the edge (wetting end) of each wood specimen so to eliminate the effect of swelling on the precision of the dynamic contact angle measurement. The average moisture content (MC) of the wood samples was approximately 6 to 7 %. Specimens for experimental use were randomly selected for a complete statistical randomization. Sitka spruce had an average specific gravity of 0.35 (g/cc). Sugar maple had a specific gravity in the range of 0.69 to 0.71; with the average of 0.70. Douglas-fir had an average specific gravity of 0.48, and quaking aspen had an average specific gravity of 0.49.

4.1.6. Swelling of Compressed Fibers in Water and Organic Liquids

Anhydrous organic liquids were used in this work. The various properties of the solvents used are shown in Table 4-5 (molar volume, cohesive energy density (CED), and hydrogen bonding parameter). The chemical classification of the organic liquids is the same with that in Chapter 4.2.2, that is: (a) Class I: High CED, low molar volume

TABLE 4-5

Organic Liquids used in Compressed Fiber Swelling Experiment

	Liquids	Molar Volume [1] (cc)	CED [2] (cal./ml.)	Hydrogen Bonding [3]
Class I.				
	Water	18.0	448	high
	Methanol	40.7	166	high
	Ethanol	58.5	123	high
	Propanol	75.0	109	high
	Formamide	39.9	308	high
	Ethylene glycol	55.8	215	high
Class II.				
	Pyridine	80.4	107	high
	Acetone	74.0	86	medium
	Dioxane	85.7	95	medium
	Methyl acetate	79.7	92	medium
	Ethyl acetate	98.5	83	medium
Class III.				
	Nitromethane	54.0	150	low
	Butyrolactone	76.8	162	medium
Class IV.				
	Ethylene dichloride	79.4	85	low
	Carbon tetrachloride	97.1	74	low
Class V.				
	Toluene	106.4	80	low
	Benzyl alcohol	103.6	120	high
Others				
	DMSO	71.0	144	high
	Acetic acid	57.1	102	high
	Butylamine	98.8	76	high

Note: 1, 2: Data from Robertson (1964); 3: Lieberman (1962).

(MV), and high hydrogen bonding parameter (HBP); (b) Class II: Medium CED, low MV, and high to medium HBP; (c) Class III: High CED, low MV, and low HBP; (d) Class IV: low CED, low MV, and low HBP; and (e) Class V: very high MV (above 100 cc). Commercial α-cellulose was provided by the Sigma Chem. Corp.. Thermomechanical pulp (TMP, loblolly pine), avicell (high crystalline cellulose), and aspen fiber (ground wood) samples were provided by the USDA Forest Products Laboratory at Madison, Wisconsin. Cotton, rayon staple, filter paper, sulfite pulp (sitka spruce), and kraft pulp (sitka spruce) samples were available or prepared in the Wood Chemistry Laboratory at the Department of Forestry, University of Wisconsin-Madison, Madison, Wisconsin.

4.2. Methods

4.2.1. Swelling of Wood at Room Temperature

Five cross-sections each of spruce, Douglas-fir, maple, and aspen, prepared as described previously (Chapter 4.1.1) were swollen in distilled water at room temperature (23° C). Two cross-sections each of spruce, Douglas-fir, maple and aspen, prepared as described previously (Chapter 4.1.2) were also swollen in various 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 dry cross-sections were transferred from the oven and cooled in a desiccator. The cooled weights and tangential dimensions were measured as quickly as possible. The maximum tangential swelling of the wood blocks in the liquids was determined in sealed weighing bottles placed in a thermostatically controlled bath (23° C) for 100 days. The maximum tangential percentage swelling was calculated by the use of the following equation:

$$\text{Percentage swelling} = \frac{(\text{Swollen Dim. - Oven Dry Dim.})}{(\text{Oven Dry Dimension})} \times 100 \qquad 4.1$$

The rate of wood swelling in water and in the organic solvents at room temperature was evaluated using a computerized linear variable displacement transformer (LVDT) apparatus (Figure 4-1) with small intervals of time (15 - 600 sec). Although a very small induction period is anticipated, the slope of the initial linear portion of the plot of tangential swelling with time (see Figures 5-3, 6-2, 6-3) was used as the estimate of the swelling rate constant, k (tangential % per minute).

4.2.2. Swelling of Wood at Elevated Temperatures

Wood swelling experiments at high temperatures were carried out with the same computerized linear variable displacement transformer (Figure 4-1). 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 three or four temperatures, except for water (23, 40, 60, 80, and 100° C); 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 (see Figures 5-1, 5-2, 6-1). Although a very small induction time was usually present, the slope of the initial linear portion of the tangential swelling

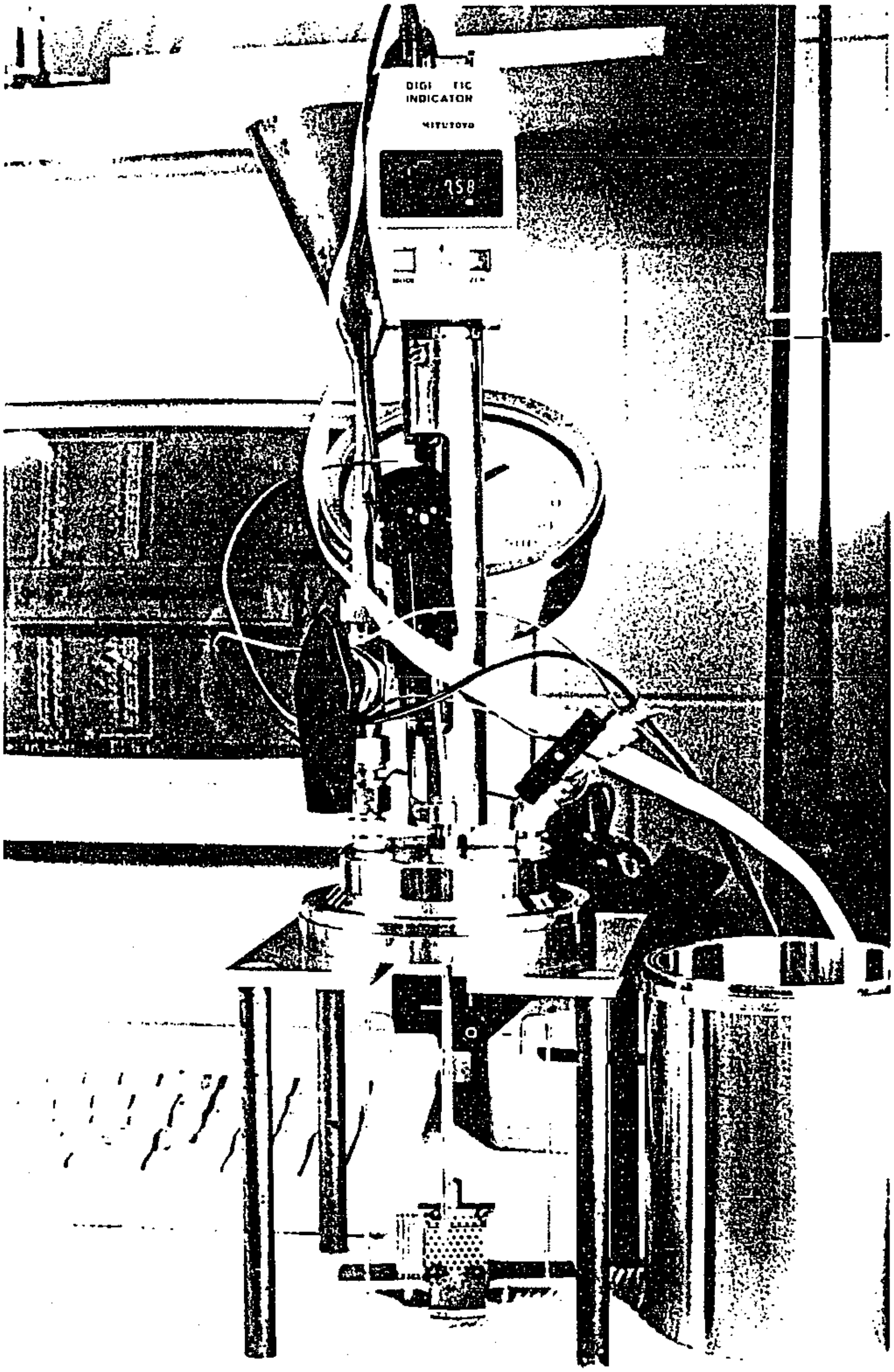

FIGURE 4-1. Swelling apparatus with computer interfaced linear variable displacement transformer.

versus time plot was used for the determination of the wood swelling rate, k. Then, from the Arrhenius equation:

$$k = A\,e^{-Ea/RT} \qquad 4.2$$

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 depending upon the temperature, swelling liquid, and wood species were utilized in order to determine the swelling rate constant k.

4.2.3. Extraction of Wood

A series of extractions were done to determine the best extraction procedure (Table 4-6). Apparently, boiling water causes significant changes in wood structure and hemicellulosic substances are removed from the cell wall. We decided thus to avoid an extraction procedure which would involve a boiling water step. An extraction with 80 % ethanol was chosen as the most suitable for our investigation since it gave the least swelling with suitable removal of the extractives (Table 4-7). The ethanol extractions were carried out for 2 hours by immersion of the wood samples in the solvent. The extracted wood samples were then oven-dried for 24 hours at 65° C. For sugar analysis the extracts were hydrolyzed with 2 ml of 3 % sulfuric acid dissolved in solvent and analyzed by high pressure liquid chromatography (HPLC) (Table 4-8).

TABLE 4-6

Extraction of Wood by Different Methods

Extraction Procedures:	**1** (%)	**2** (%)	**3** (%)	**4** (%)	**5** (%)	**6** (%)
<u>Weight Changes</u>						
Sitka Spruce	-6.9	-6.9	-3.8	-1.1	-0.1	-1.6
Douglas-fir	-2.5	-3.5	-2.2	0.4	-0.6	0.3
Sugar Maple	-5.8	-5.1	-0.6	0.5	-0.4	-0.1
Quaking Aspen	-3.2	-4.1	-1.5	-0.2	-0.1	-1.8
<u>Tangential Dimension Changes</u>						
Sitka Spruce	-2.8	-1.9	-0.5	-0.6	0.4	-0.3
Douglas-fir	1.1	0.3	0.6	0.2	0.5	0.1
Sugar Maple	-2.7	1.6	1.7	0.9	0.3	0.8
Quaking Aspen	-0.9	-0.7	-0.3	0.2	0.7	0.4

<u>Note:</u> (+ , positive): % of swelling or weight gain.

(- , negative): % of shrinkage or weight loss.

1: Extraction with Benz/EtOH (2:1); boiling water; Acet./Water (9:1); 4+4+4 hrs.

2: Extraction with Benz/EtOH (2:1); boiling water; 4+4 hrs.

3: Extraction with Benz/EtOH (2:1); 95% ethanol; boiling water; 4+4+4 hrs.

4: Extraction with Benz/EtOH (2:1); Acet./Water (9:1); 4+4 hrs.

5: Extraction with Benz/EtOH (2:1); 4 hrs.

6: Extraction with Benz/EtOH (2:1); 95% ethanol; 4+4 hrs

TABLE 4-7

Extraction of Wood with 80 % Ethanol for Two Hours

Wood Species	**Weight Change** (%)	**Tangential Dim. Change** (%)	**Radial Dim. Change** (%)	**Longitudinal Dim. Change** (%)
Sitka Spruce	- 3.6	- 1.2	- 1.1	1.3
Douglas-fir	- 2.5	- 0.6	- 0.9	1.1
Sugar Maple	- 2.4	- 0.6	- 0.8	1.2
Quaking Aspen	- 2.1	- 0.2	- 0.7	2.4

Notice: (- , negative) : weight loss or % of shrinkage

(+ , positive) : % of swelling

TABLE 4-8

Sugar Composition (HPLC) of Ethanol (80 %) Extracts from Wood

Species	Glucose	Mannose	Galactose	Xylose	Arabinose *
Q. Aspen	38.2	4.0	8.5	9.1	40.1
S. Maple	76.0	3.3	3.2	2.8	54.3
S. Spruce	2.6	1.6	9.0	2.2	84.6
Douglas-fir	4.3	4.7	22.0	14.7	14.8

* Rhamnose was not resolved from the arabinose peak but rhamnose is less than 10% of the combined arabinose/rhamnose total.

4.2.4. Wetting of Wood

Some of the first notions of the relationship between surface energy and contact angle for a liquid drop on a solid surface were expressed by Young's equation (1805):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \qquad 4.3$$

where: γ_{SV} : Interfacial surface tension between solid and vapor

γ_{SL} : Interfacial surface tension between solid and liquid

γ_{LV} : Interfacial surface tension between liquid and vapor

θ : Contact angle

Later, Dupre' (1869) developed an equation for the thermodynamic energy of interaction, which is widely known as the work of adhesion, W_A:

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \qquad 4.4$$

Hence, combining Eqs. 4.3 and 4.4 we get the following equation:

$$W_A = \gamma_{LV} (1 + \cos\theta) \qquad 4.5$$

where: γ_{LV} : surface tension of the liquid

θ : contact angle formed between liquid and substrate

Thus the thermodynamic energy of interaction at an interface can then be calculated from the contact angle and the liquid surface tension. The Wilhelmy equation (1863) allows the calculation of the contact angle θ in order to compute the work of adhesion (W_A):

$$F_W = P\,\gamma_{LV}\,\cos\theta \qquad 4.6$$

where: F_W : Wetting force (excluding the buoyancy force)

γ_{LV} : Surface tension of liquid

P : Perimeter of substrate

θ : Contact angle formed between liquid and substrate

Fowkes (1962) has proposed that the total work of adhesion, W_A, can be divided into parts corresponding to various contributions from different interactions such as dispersive forces, hydrogen bonding, acid-base, dipole-dipole, and induced dipole interactions. However, he suggested (1978) that polar forces are very small and hydrogen bonding is a form of acid-base interactions such that,

$$W_A = W_A^d + W_A^{ab} \qquad 4.7$$

where: W_A^d : Dispersion component of the work of adhesion

W_A^{ab} : Acid-base component of the work of adhesion

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

$$W_A^d = 2\,(\gamma_S^d\;\gamma_{LV}^d)^{1/2} \qquad 4.8$$

where: γ_S^d and γ_{LV}^d are dispersion components of the surface energies of the solid and liquid respectively.

If we consider here that the adsorption of the vapor of the probe liquid is negligible, then the dispersion component of the surface tension, γ_S^d, of the solid can be measured with a neutral, nonself-associating liquid using the following equation:

$$\gamma_S^d = \gamma_{LV} (1 + \cos\theta)^2 / 4 \qquad 4.9$$

where: $\gamma_{LV} = \gamma_{neutral}$: Surface tension of the non-self-associating liquid

θ : Contact angle between the non-self-associating liquid and the substrate

Methylene iodide (diiodomethane) was used as the dispersive probe liquid to obtain γ_S^d in this experiment. The dispersion component of the liquid can be calculated with a solid surface which has only dispersive interactions or more precisely, from interfacial tensions of a polar liquid against a neutral hydrocarbon. It is important to note here that the polar contribution to the surface energy, γ_S^p, is a very inadequate measure of polarity or hydrophilicity. It should be also noted by Fowkes (1991) that the acid-base work of adhesion (W_A^{ab}) can be calculated from the molar heats of acid-base interaction between the two materials, or by measuring the surface basicity and surface acidity components of the acid-base surface tension of the phases involved (Oss, 1988). The acid-base contributions to the work of adhesion are determined using a Lewis base such as formamide and a Lewis acid such as ethylene glycol with Eq. 4.8 and 4.9, and then from Eq. 4.7 rewritten as:

$$W_A^{ab} = W_A - W_A^d \qquad 4.10$$

All wetting force measurements were done with a CAHN Dynamic Contact Angle Analyzer (Figure 4-2) with an IBM 3865X for data acquisition and analysis. Contact angle measurements were done by the Wilhelmy method based on the following equation:

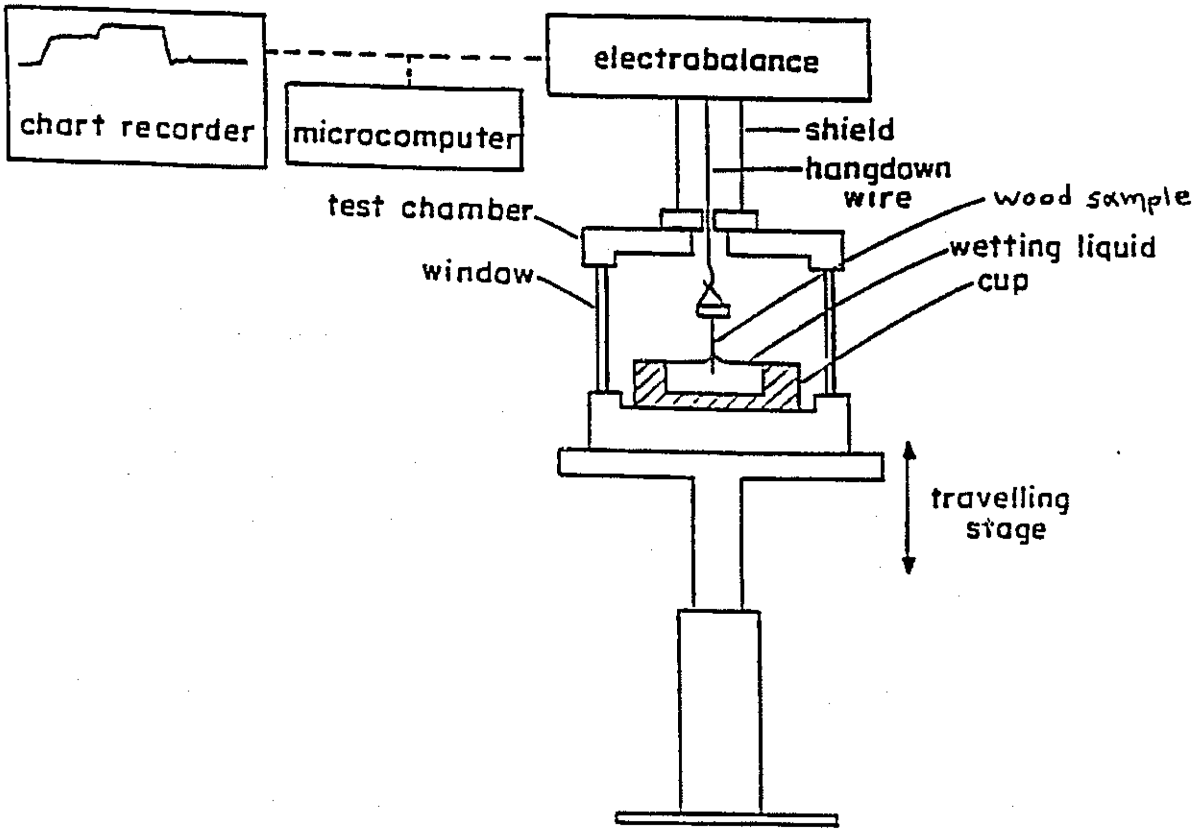

FIGURE 4-2. Schematic diagram of CAHN Dynamic Contact Angle Analyzer.

$$F = \gamma_{LV} P \cos\theta - \delta_l g A h \tag{4.11}$$

where F is the wetting force, γ_{LV} is the liquid surface tension, P is the sample perimeter, δ_l is the liquid density, g is the gravitational constant, A is the cross sectional area of the wood sample, and h is the depth of immersion of the sample. Average "advancing" force values minus the buoyancy force were then used to calculate the advancing contact angle and the work of adhesion. A typical run is performed by placing a small wood sample in the electrobalance (Figure 4-2) and raising a beaker of wetting liquid with a small elevator until the liquid contacts the sample. The elevator speed was controlled at 150 microns per second and wetting force readings were obtained on a microcomputer. In the plot of the wetting force F versus depth of immersion h, a simple extrapolation gives the cosine of the advancing contact angle ($\cos\theta_A$) since the liquid surface tension (γ_{LV}) and wood sample perimeter (P) are known as shown in Figure 4-3 for sugar maple in pyridine. Formamide was used to find the acidic character of the wood surface and ethylene glycol was used to probe the basic properties. W_A^{ab} of the work of adhesion was evaluated for all wood species. Diiodomethane was used for the calculation of the Lifshitz-van der Waals forces of the wood surfaces. Hexadecane, which has a very low surface tension, was used for measuring the wood sample perimeter, P. Distilled water was used to find water wettability and water contact angles. In addition, all thirty organic liquids were used for wetting measurements with two wood species, sitka spruce (softwood) and sugar maple (hardwood), and specific wettabilities of these two wood species in the organic liquids were evaluated (using the advancing contact angle). Advancing specific wettability, W_S, is defined by the following equation:

$$W_S = \gamma \cos\theta \tag{4.12}$$

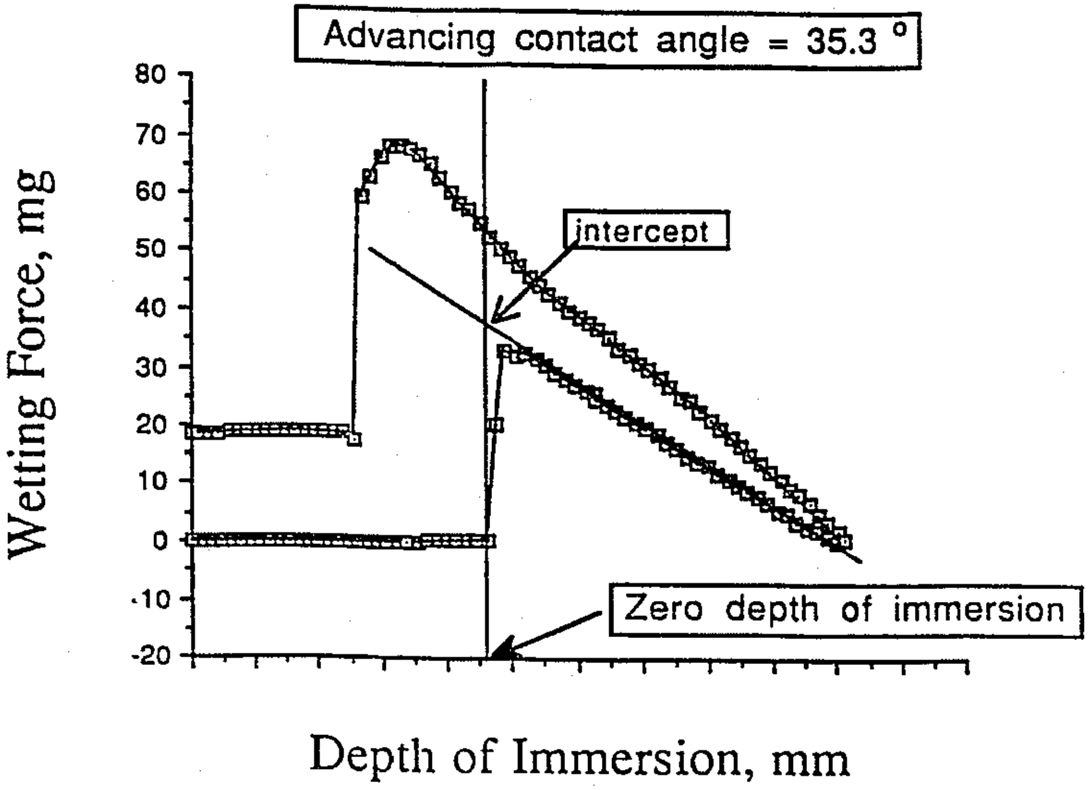

FIGURE 4-3. Wetting force as a function of depth of immersion for sugar maple in pyridine.

where: γ is the liquid surface tension and θ is the advancing contact angle.

Wu's simultaneous equations (1971) were used to calculate the γ_S^d and γ_S^p of the wood surfaces using wetting measurements with water (polar) and methylene iodide (neutral). These two liquids were used by Owens and Wendt (1969) in conjunction with an extended form of Fowkes equation (1965). In this work, Wu's equation (Wu, 1971) was rearranged to two simultaneous equations, one for water and another for methylene iodide.

4.2.5. Swelling of Compressed Fibers in Water and Organic Liquids

In our experiment the following parameters were considered:

Condition of reaction	Structure of fiber sample	Swelling liquid
Room temperature (23°)	Pellet bulk density	Molar volume
Elevated temperatures	Type of fiber (pulps, cotton, α-cellulose, etc.)	CED
		Hydrogen bonding

All samples (except for α-cellulose and avicell) were first dried at 65° C for 24 hours. After drying, the samples were placed in a die mold and compressed with a hydraulic press (Carver Laboratory Press) under various loads for thirty seconds so that a range of bulk densities could be obtained. Each fiber pellet sample weighed about 0.6 grams. In some instances, it was necessary to reduce slightly the sample size in order to achieve the desired bulk density. All samples were then permitted to recover for 24 hours in a dessicator (sodium aluminosilicate). To determine the bulk density of a fiber pellet at the start of the testing, the sample weight was determined with a scale to ± 0.001 gm and the sample thickness was measured with an accurate digimatic caliper to ± 0.001 cm. The density was calculated by the formula of a cylinder. For the room temperature experiments, the swelling liquid was placed in a glass cylindrical column. A dry compressed fiber pellet was then placed carefully on the bottom of a graduated pipette with small holes in the bottom. The diameter of the pipette was slightly larger than that of the pellet (roughly 1.3 cm). The pipette was then inserted slowly into the glass column. The swelling liquid immediately penetrated the pipette from the bottom and came in contact with the fiber sample and swelled it upwards. The expansion of the fiber pellet was in most cases very quick. On first contact with the liquid, bulk densities are subject to drastic changes as the dimensions change. After 24 hours of swelling, the external dimensional change of the fiber pellet was measured with the digimatic caliper. The percentage increase in the thickness direction was taken as the maximum liquid-holding capacity in the particular solvent (maximum fiber pellet swelling). All measurements were done at room temperature. Each experiment was replicated twice.

At elevated temperatures, compressed fiber swelling experiments were carried out in an apparatus described previously (Chapter 4.2.1) using the same computer linear variable displacement transformer (Figure 4-1) which in this experiment was modified to increase sensitivity (very light aluminum gauge and highly sensitive low-pressure digimatic indicator). In a typical experiment, fiber pellets of a bulk density of about 1.0 g/cc were inserted in the apparatus which was immersed in a constant temperature oil bath. Each pellet sample was placed in a stainless steel cylindrical holder (diameter about 1.4 cm) 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, pellet swelling rate measurements were made at three temperatures (23, 40, and 60° C). A fresh aliquot of liquid was used at each investigated temperature.

Fiber pellet dimensional increases were continuously measured by computer until equilibrium was attained (see Figure 9-4). The slope of the initial linear portion of the fiber pellet swelling increase versus time plot was used for the determination of the swelling rate (Chapter 4.2.1). Then, from the classical Arrhenius equation (Eq. 4.2) plots of ln k versus 1/T gave the activation energies for pellet fiber swelling, E_a. Small intervals of time (1 - 15 sec) depending upon the temperature, swelling liquid, and type of fiber were utilized in order to determine the swelling rate constant k.

CHAPTER FIVE

SWELLING OF WOOD IN WATER

5.1. Introduction

The swelling of wood, as manifested by the external dimension changes, varies with the species, structure, density, drying conditions, etc. The swelling of wood in both liquid water and water vapor has been studied extensively for the past fifty years. A number of scientists have made attempts to determine the factors that influence wood swelling in liquid water (Schwalbe et al., 1931; Saechtling et al., 1934; Stamm, 1935; Nayer 1948; Stamm, 1964; Hossfeld, 1972). Surprisingly, accurate kinetic data on the wood swelling in water has not yet been reported. In this study the important factors to wood swelling in water at room temperature as well as at elevated temperatures have been evaluated.

5.2. Results and Discussion

Figure 5-1 is a graph of a swelling profile of sitka spruce. The increase in the tangential dimension in mm is plotted against time (min). A very small induction period is noted on the graph. This induction period was also noted by West (1988) in his study of the swelling of wood in organic solvents. 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. owever, 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.

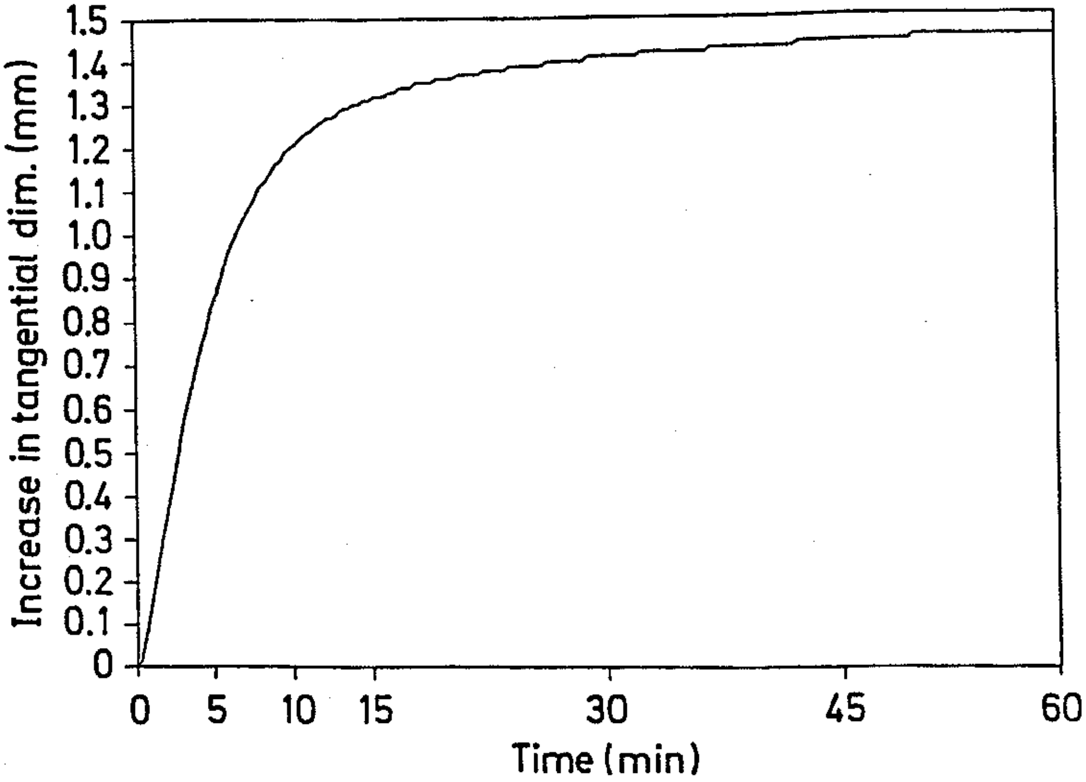

FIGURE 5-1. Swelling of sitka spruce in water at 23° C.

To accommodate this induction period, West and Banks (1989) calculated a time to one-half swell ($t_{1/2}$). The maximum equilibrium swelling is reached after about six hours of swelling in water at 23° C.

Figure 5-2 is a typical plot of the percent tangential swelling versus time (hrs) for quaking aspen. Even at room temperature (23° C), there is a very rapid swelling of wood in water as noted in the initial linear portion of the plot. Figure 5-3 is a detailed plot of this initial linear portion of the plot but at an interval time of fifteen seconds. A swelling rate constant, k, is then derived from the slope of this curve. The activation energies, Ea, are then calculated from the standard Arrhenius equation (Eq. 4.2) with a typical plot shown in Figure 5-4, in this case for sitka spruce in water.

5.2.1. Maximum Swelling of Wood in Water

The results in Table 5-1 show the maximum tangential swelling, the rate of swelling, and the activation energies of unextracted wood in water at various temperatures. The total time of swelling is the time required to reach an apparent equilibrium and is presented in the parentheses. The results show the tremendous increase in the rate of swelling of wood that takes place as the temperature is increased up to 100° C. The temperature dependence of wood swelling in water very closely obeyed the Arrhenius equation which strongly suggests that the phenomenon of wood swelling is an activated process similar to a classical chemical reaction. The strong correlation between the hydrogen bonding ability of a liquid and its swelling capacity for wood noted previously by Stamm (1964), suggests a hydrogen bond breaking mechanism for wood swelling. A bimolecular process is most likely, whereby the liquid forms a transition state with the hydrogen bonded hydroxyl groups in wood (West, 1988). The transition state then collapses to give a molecule of liquid attached by a

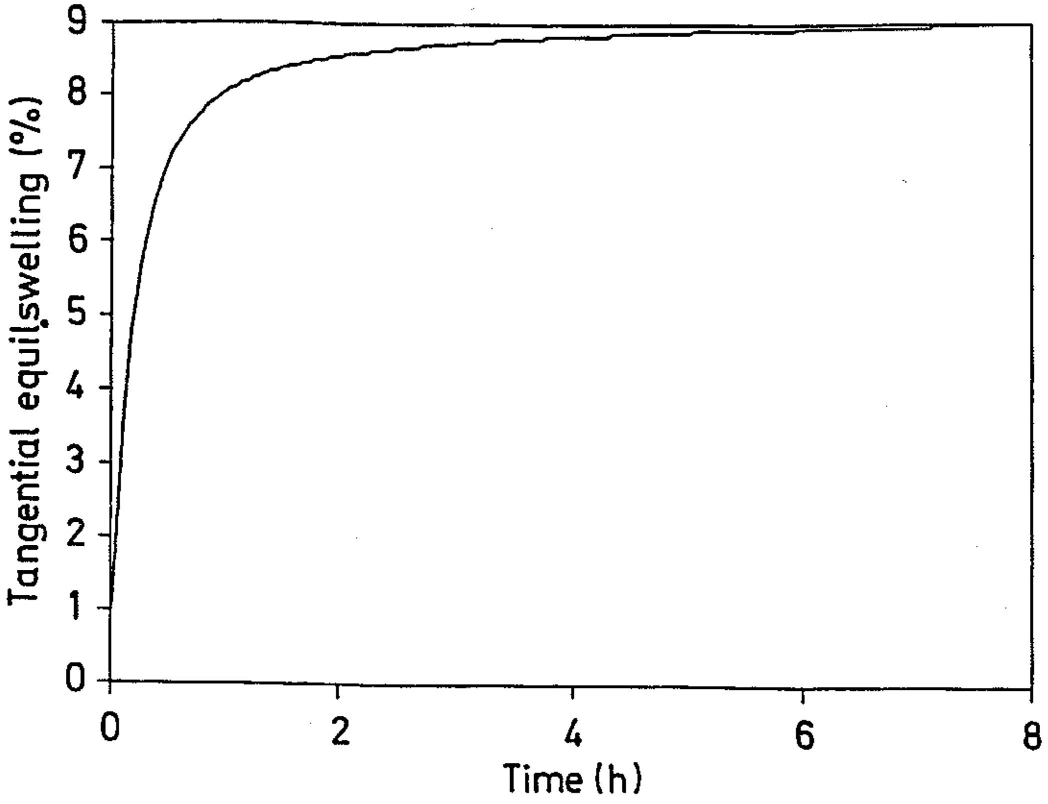

FIGURE 5-2. Swelling of quaking aspen in water at 23° C.

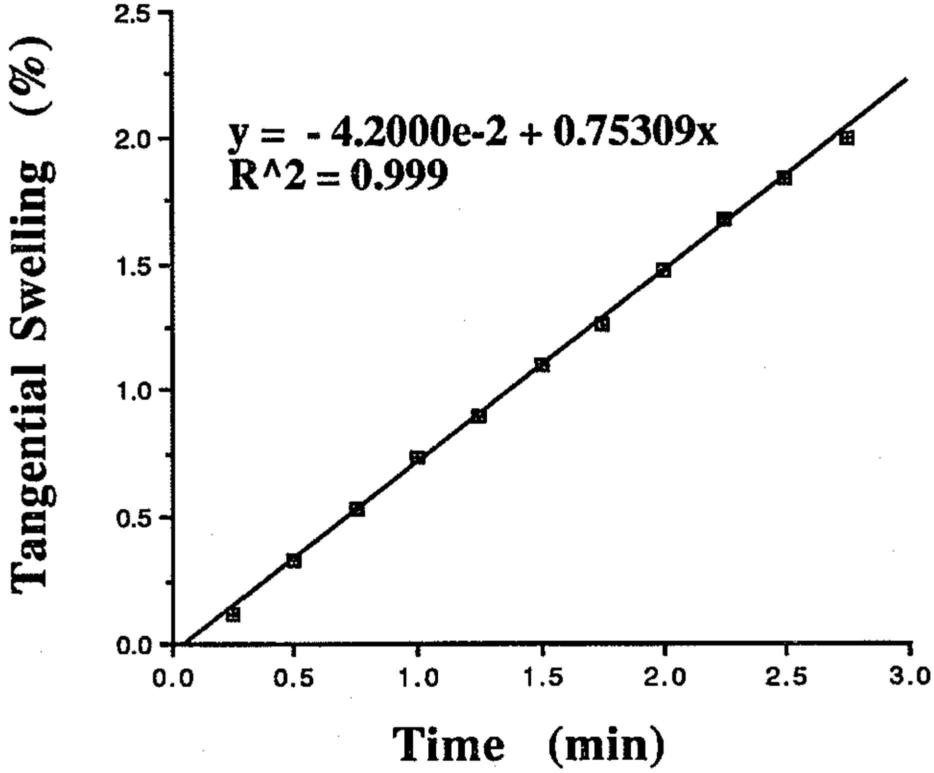

FIGURE 5-3. Initial linear swelling of quaking aspen in water at 23° C.

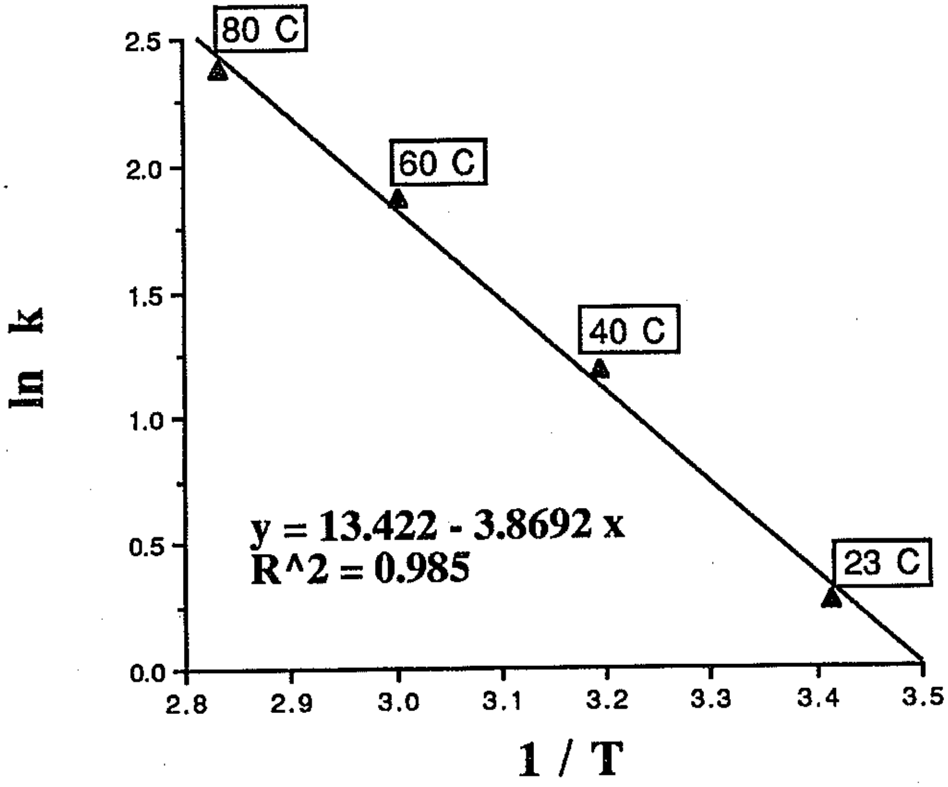

FIGURE 5-4. Plot of ln k versus 1/T for calculation of activation energy of swelling of sitka spruce in water.

TABLE 5-1

Rates of Swelling, Maximum Tangential Swelling Values, and Activation Energies of Wood Swelling in Water

Maximum Tangential Swelling, (%) (Std.Deviation; Time, hrs)	Spruce	D.Fir I	D.Fir II	Maple	Aspen
Temperature (°C)					
23	6.5 (0.4; 1)	7.6 (0.2; 8)	8.7 (0.2; 8)	10.0 (0.4; 2)	9.1 (0.1; 8)
40	6.9 (0.4; 1)	7.7 (0.2; 5)	8.8 (0.2; 5)	10.8 (0.4; 1)	8.9 (0.2; 3)
60	6.9 (0.2; .5)	7.7 (0.2; 3)	9.0 (0.2; 3)	11.5 (0.3; .7)	9.4 (0.2; 2)
80	7.2 (0.3; .3)	8.0 (0.3; 2)	9.1 (0.2; 2)	11.5 (0.4; .5)	9.6 (0.3; 1)
100	7.3 (0.4; .2)	8.1 (0.2; 2)	9.3 (0.2; 2)	12.3 (0.4; .3)	10.1 (0.2; .7)
Swelling Rate, k, (%/min)					
23	1.3	0.3	0.7	0.3	0.8
40	3.3	0.9	1.4	1.1	2.1
60	6.5	1.8	3.1	3.6	5.9
80	10.8	4.7	4.2	6.6	14.4
100	14.8	6.9	5.8	7.6	20.4
Activation Energy, Ea, (KJ/mole)	32.2	38.9	33.0	47.6	44.7

hydrogen bond to wood. Therefore liquids with strong hydrogen bonding potential would be expected to swell wood to the greatest extent. Evaluation of surface free energies of various wood species with a variety of liquids should provide valuable information for interpretation of swelling mechanisms of wood.

The equilibrium time significantly decreases as the temperature is raised, for instance, with aspen, it decreased from 8 hours at 23° to 40 minutes at 100°C. The data show that the equilibrium swelling of hardwoods in water was greater than that of softwoods (spruce averaged from 6.5 to 7.3 %, Douglas fir from 7.3 to 9.3 %; sugar maple varied from 10.0 to 12.4 % and aspen from 9.1 to 10.0 %). This is very likely due to the higher density of hardwoods. A relatively linear relationship is shown for plots of the maximum tangential swelling both within (Figure 5-5) and between (Figure 5-6) wood species versus wood density at 23° C. This is consistent with Stamm's earlier work (Stamm, 1964).

5.2.2. Activation Energy of Wood Swelling in Water

The higher density hardwoods had much greater activation energies for swelling in water than those of the low density softwoods (Table 5-1). The Ea for the hardwoods ranged from 44.0 - 47.6 KJ/mole, while the Ea for the softwoods was in the range of 32.2 - 38.9 KJ/mole. Using some of Stamm's earlier published data on swelling of Sitka spruce in water, we calculated an Ea of 36.4 KJ/mole (Stamm, 1952) in good agreement with the results reported in this work. In another study by Stamm (1959) on the related process of bound water diffusion in wood, an Ea of 50.2 KJ/mole was calculated from the variation of the diffusion coefficient with temperature in the range of 3.5 - 56.5° C. The reasonable agreement of the activation energies obtained by the different methods verifies the relationship between diffusion and swelling.

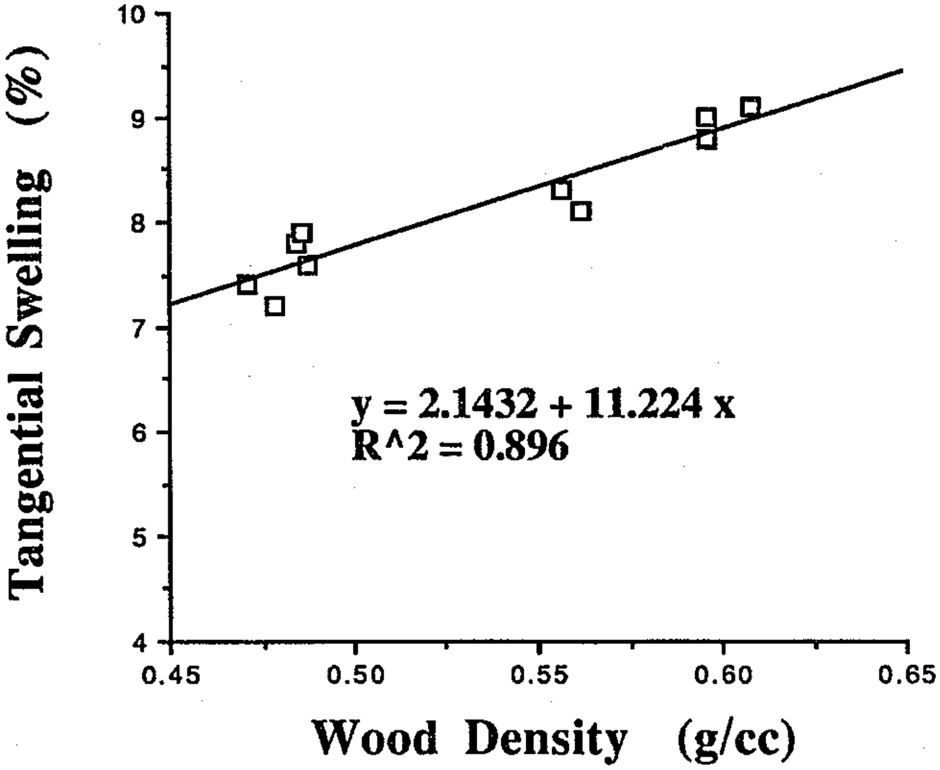

FIGURE 5-5. Maximum tangential swelling of Douglas-fir in water at 23° C versus wood density.

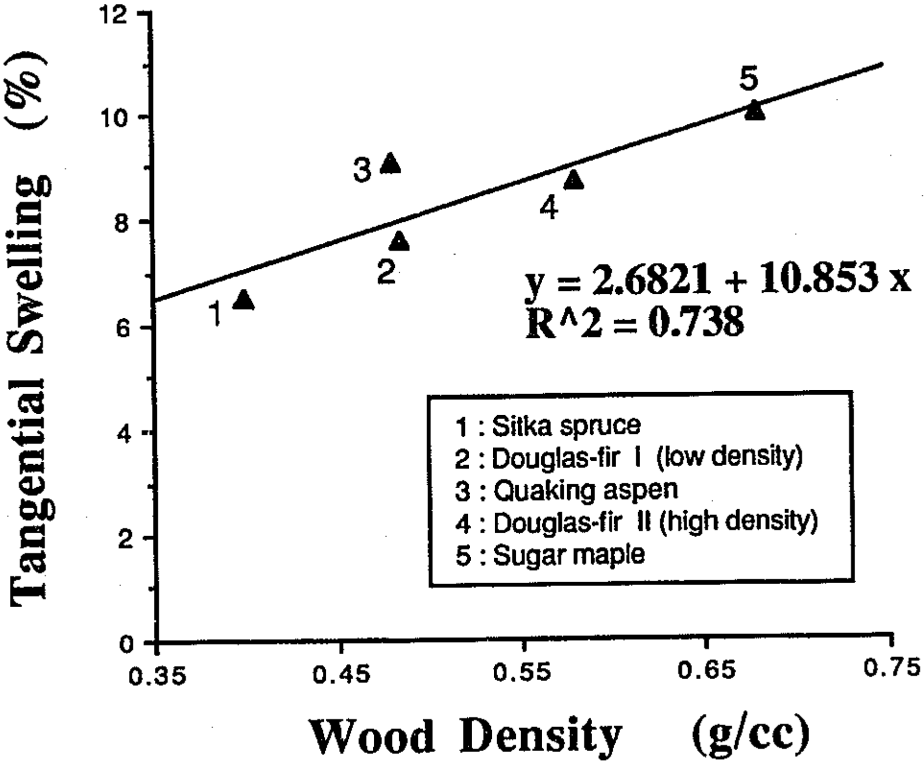

FIGURE 5-6. Maximum tangential swelling of wood in water at 23° C versus wood density.

It should also be noted that the maximum tangential swelling also increases slightly as the swelling temperature is increased as shown in Figure 5-7. This may be linked to minor changes in the cell wall structure when wood is treated with high temperature liquids. This will be further discussed in section 7.2.1.

5.3. Summary

Activation energies for the swelling of wood in water were evaluated for the first time. Raising the water temperature above room temperature significantly increased the rate of swelling of wood. The strict linear dependence of swelling on the temperature suggests a chemical mechanism. The activation energies obtained from Arrhenius plots ranged from 32.2 KJ/mole for sitka spruce to 47.6 KJ/mole for sugar maple. Although the two hardwoods exhibited greater maximum tangential swelling compared with the two softwoods, the maximum swelling appears to be correlated with the wood density. Also, an increase in water temperature caused a slight increase in the maximum tangential swelling of wood (5 - 10 %).

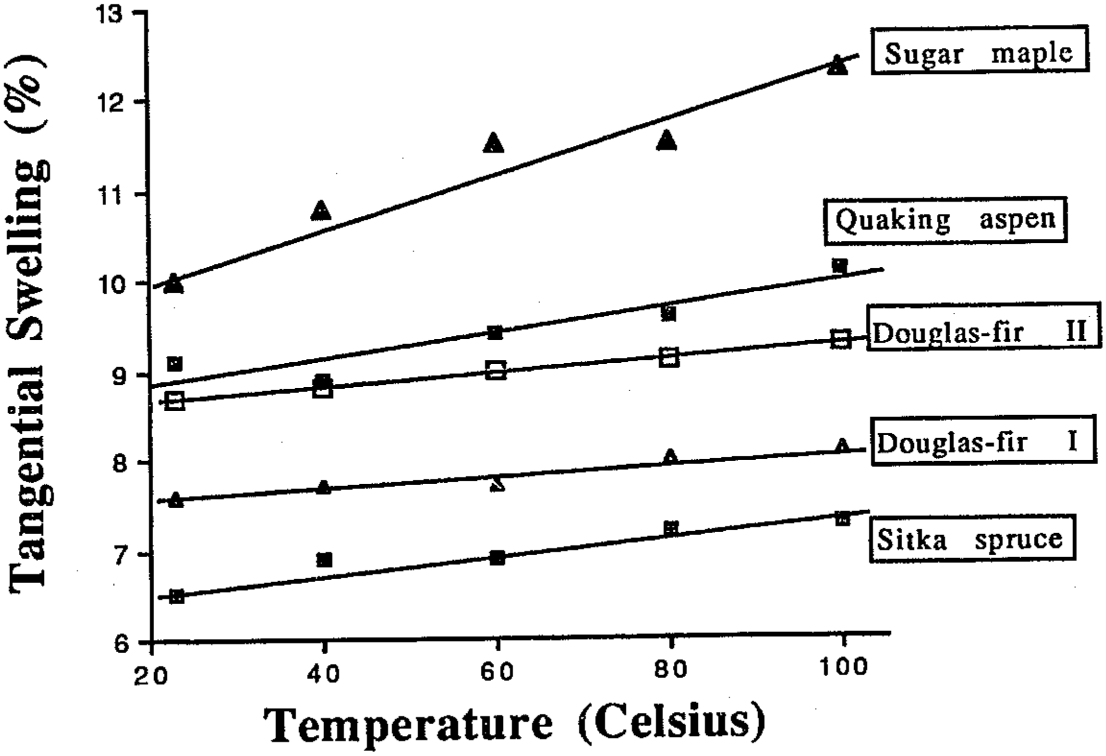

FIGURE 5-7. Maximum tangential swelling of wood in water versus temperature.

CHAPTER SIX

SWELLING OF WOOD IN ORGANIC LIQUIDS

6.1. Introduction

The swelling of wood in liquids is a complex process which is strongly influenced by both the solvent and the wood substrate. This investigation was designed to ascertain the important factors to wood swelling in an extensive series of organic liquids. In Chapter 5, we evaluated the relative effects of factors such as wood density, extractives, and temperature to wood swelling in water. In this chapter, we investigate 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. Most of the previous works have 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 (activation energy of wood swelling) on the rate and maximum swelling of wood in a variety of organic liquids has also been ascertained.

6.2. Results and Discussion

Figure 6-1 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 equilibrium swelling is reached after about seven hours of swelling. Figure 6-2 is a

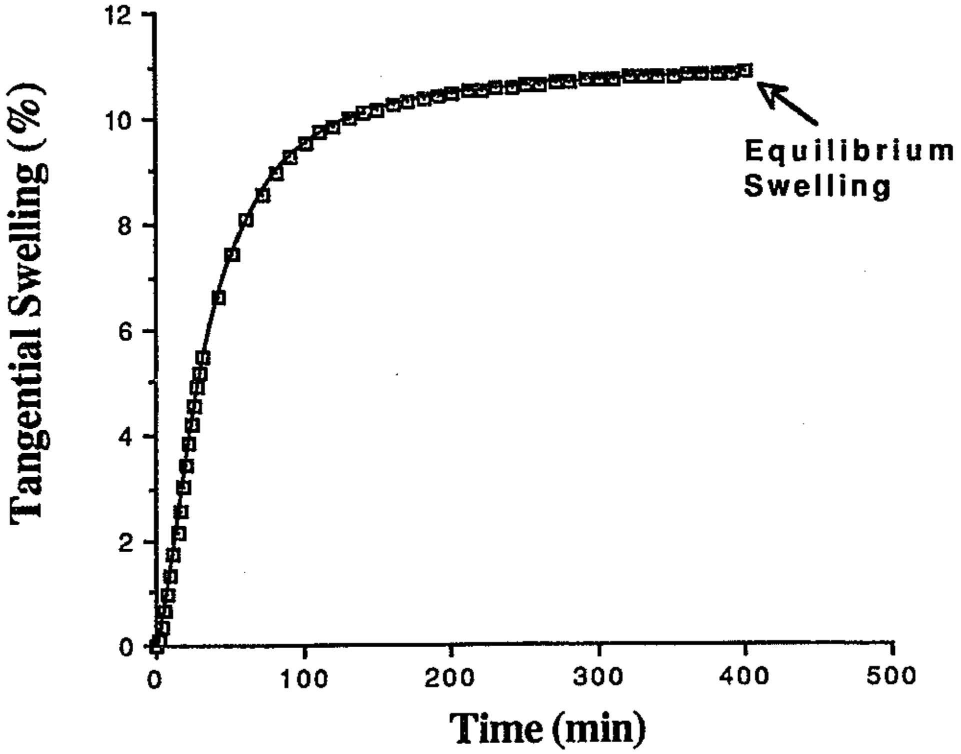

FIGURE 6-1. Schematic swelling profile of quaking aspen in pyridine at 23° C.

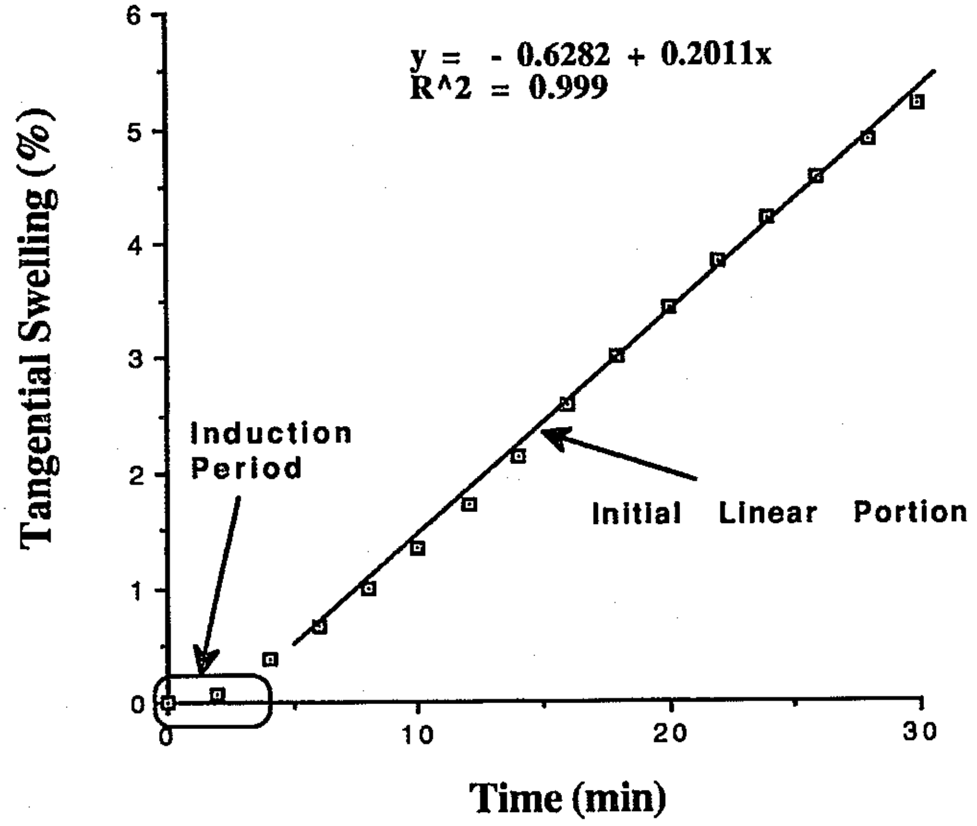

FIGURE 6-2. Initial linear swelling of quaking aspen in pyridine at 23° C.

detailed plot of the initial linear portion of the Figure 6-1 (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. In this work, the initial linear slope of the swelling profile was taken as an estimate of the wood swelling rate (Figures 6-1, 6-2, 6-3) (Chapter 5.2). Stamm (1956) in his work on the diffusion of liquids into cellulosic materials noticed that, after the induction period, the initial 2/3 portion 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 = 0.201 %/min). Figure 6-3 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 liquids at room temperature.

6.2.1. Maximum Tangential Swelling of Wood in Organic Liquids

The data presented in Table 6-1 show the maximum tangential swelling of all wood species in the anhydrous organic liquids at 23° C 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

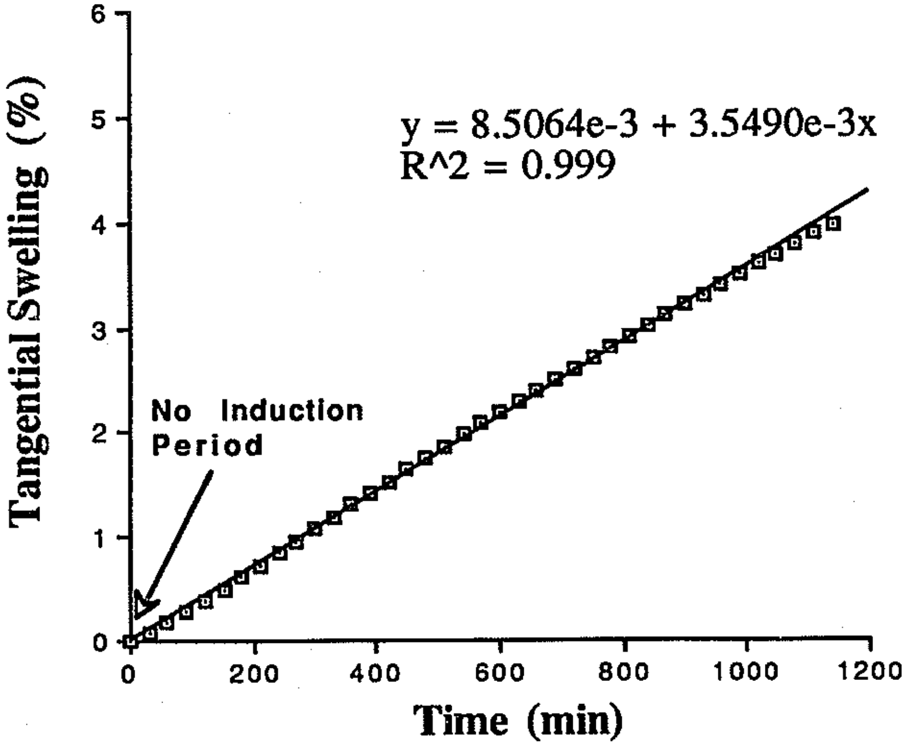

FIGURE 6-3. Initial linear swelling of Douglas-fir II (higher density) in ethylene glycol at 23° C.

TABLE 6-1 (continued)

Maximum Tangential Swelling of Wood at 23° C at the end of 100 days

	Spruce		Douglas-fir I		Douglas-fir II		Maple		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)	1.2	(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)										
Chroroform	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)

TABLE 6-1

Maximum Tangential Swelling of Wood at 23° C at the end of 100 days

(Standard deviations in parentheses)

	Spruce		Douglas-fir I		Douglas-fir II		Maple		Aspen	
(class V)										
Benzaldehyde	1.0	(0.1)	0.9	(0.1)	1.2	(0.1)	2.1	(0.1)	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	(0.3)
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	(0.5)	20.3	(0.6)	17.0	(0.3)
Acetic	8.7	(0.1)	7.6	(0.2)	9.3	(0.3)	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	(0.2)	12.4	(0.4)	11.0	(0.2)	10.6	(0.2)
Butylamine	14.5	(0.4)	16.4	(0.3)	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	(0.3)	11.6	(0.3)	12.8	(0.4)	11.9	(0.3)	11.7	(0.4)
Piperidine	0.9	(0.0)	0.62	(0.0)	0.6	(0.0)	4.3	(0.1)	12.3	(0.3)

would be expected for wood swelling in anhydrous formic acid. Quinoline, octane, butyraldehyde, nitrobenzene, carbon tetrachloride, benzyl benzoate, and piperidine (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.

Table 6-2 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, lutidine, benzaldehyde, benzyl alcohol, and 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 very good agreement with Nayer's (1948) and Stamm's (1964) work. From Tables 6-1 and 6-2, 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 (Figure 6-4) and acetates (Figure 6-5). It is apparent that, as the solvent molecule becomes bulkier, the wood maximum swelling decreases constantly (within a homologous series). In Figure 6-4, 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

TABLE 6-2 (continued)

Maximum Tangential Swelling Relative to that in Water at 23° C

	Spruce	Douglas-fir I	Douglas-fir II	Maple	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)					
Chroroform	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

TABLE 6-2

Maximum Tangential Swelling Relative to that in Water at 23° C

	Spruce	Douglas-fir I	Douglas-fir II	Maple	Aspen
Water	100.0	100.0	100.0	100.0	100.0
(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

Note: Each point is the average of two replicates.

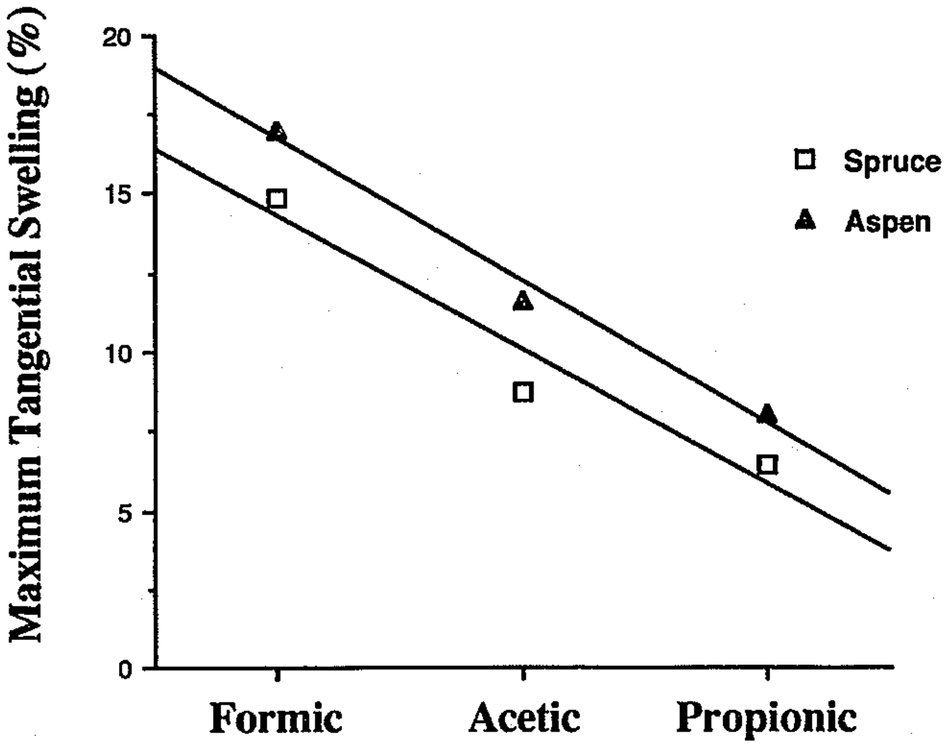

FIGURE 6-4. Maximum tangential swelling of wood in organic acids.

Note: Each point is the average of two replicates.

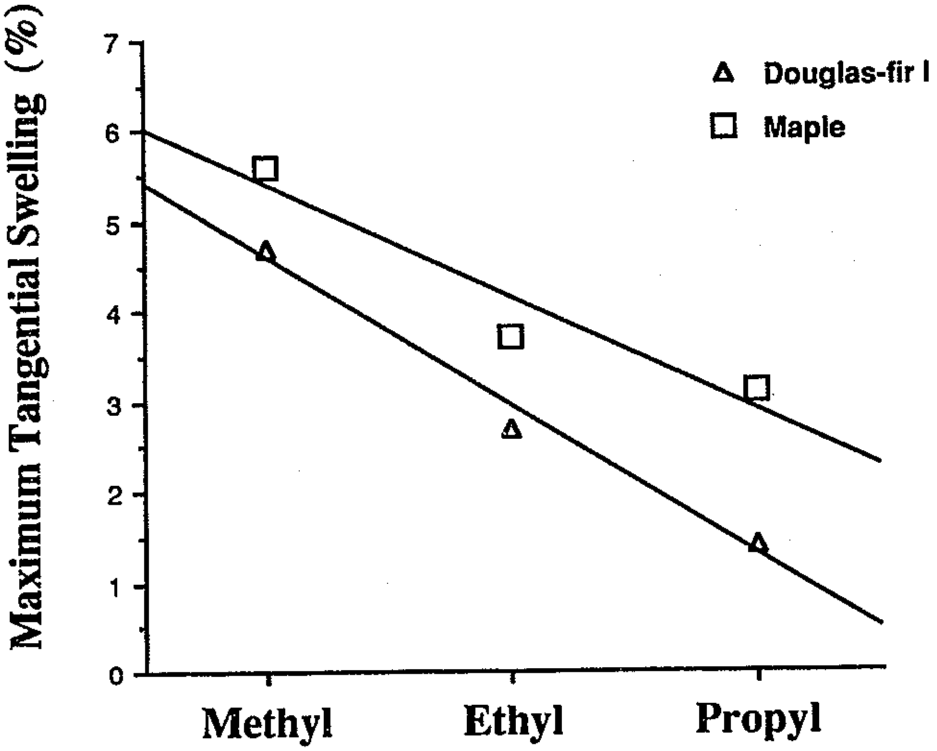

FIGURE 6-5. Maximum tangential swelling of wood in acetates.

maximum tangential 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 (Figure 6-6). 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 ΔH-value in kcal/mol for the interaction of a 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 eighteen solvents with DN data for the maximum wood swelling (Figure 6-6). 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 an acidic character. As shown in Table 6-3, 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. Such wood wetting results will be further discussed in Chapter 8.

6.2.2. Rate of Swelling of Wood in Organic Liquids at Room Temperature

In Table 6-4 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 6-4 that some organic solvents swell wood at an extremely slow rate. Such solvents include piperidine, dibutylamine, 2, 6 dimethylpyridine, quinoline, benzyl benzoate, benzyl alcohol, isopropyl ether, toluene, nitrobenzene, benzaldehyde, carbon tetrachloride, ethylene dichloride, chloroform, propyl acetate, and butyraldehyde. The fastest swelling rates were obtained with methanol, ethanol, water, butylamine, formic acid,

* DN data available for eighteen of our solvents.

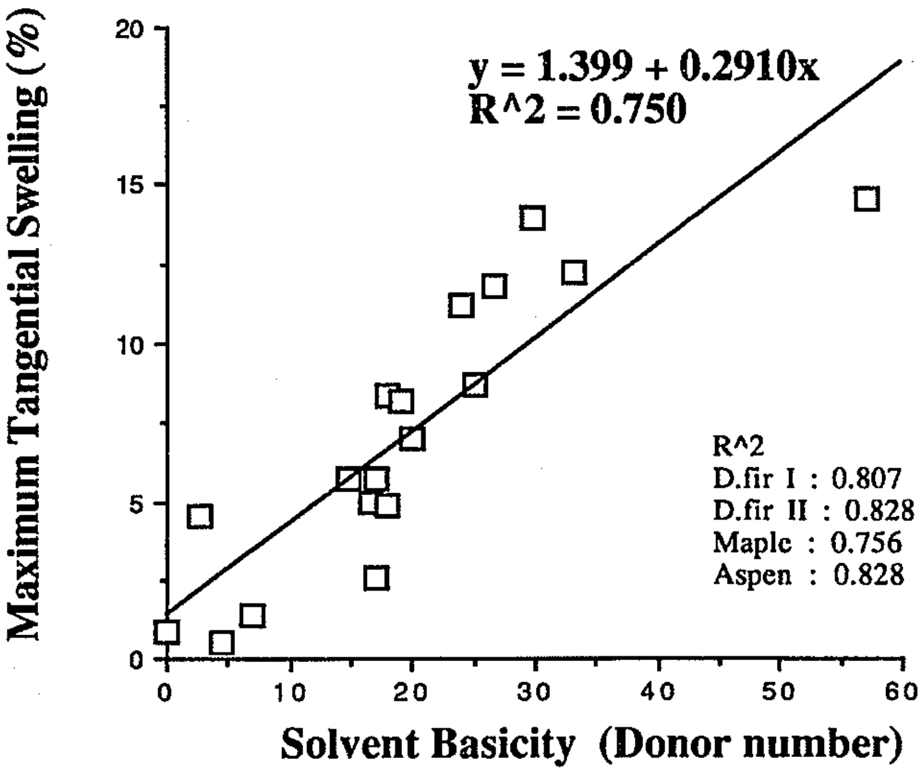

FIGURE 6-6. Maximum tangential swelling of sitka spruce plotted against solvent basicity. *

TABLE 6-3

Work of Adhesion of Wood with Various Liquid Probes

	Water	Ethylene glycol	Formamide
	(Bi-functional)	(Acidic)	(Basic)
	W_A, (dynes/cm); (θ)	W_A^{ab}, (dynes/cm)	W_A^{ab}, (dynes/cm)
Species			
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

TABLE 6-4 (continued)

Rates of Swelling of Wood in 40 Organic Solvents at Room Temperature

	Spruce	Douglas-fir I	Douglas-fir II	Maple	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

TABLE 6-4

Rates of Swelling of Wood in 40 Organic Solvents at Room Temperature

	Spruce	Douglas-fir I	Douglas-fir II	Maple	Aspen
(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

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 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 (Figure 6-7). This trend was consistent for all wood species. In addition, a consistent trend was found between the ln k and the molar volume of the swelling solvent (Figure 6-8). Figure 6-8 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 6-8. In Figure 6-9, 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.

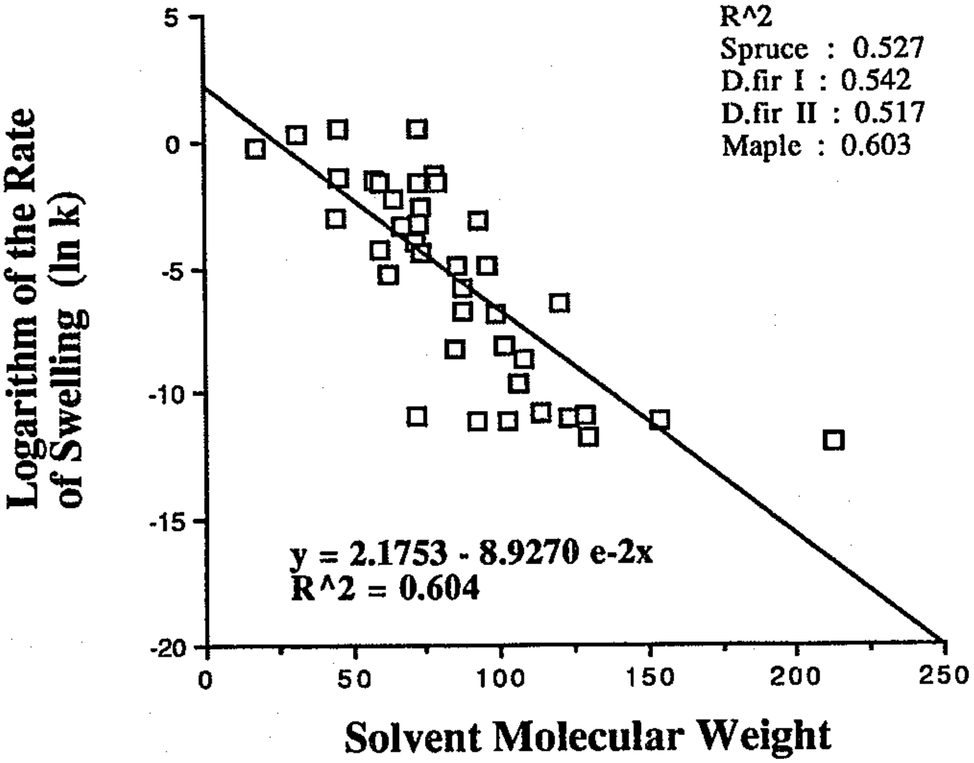

FIGURE 6-7. The logarithm of the rate of swelling of aspen plotted against the solvent molecular weight.

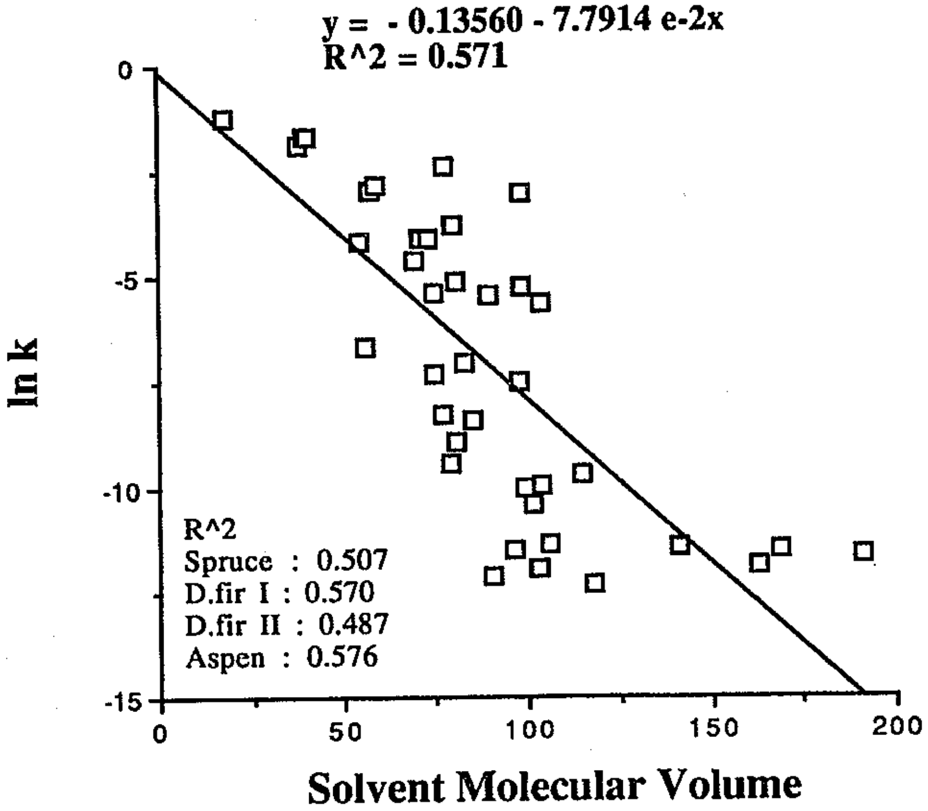

FIGURE 6-8. The logarithm of the rate of swelling of maple plotted against the solvent molecular weight.

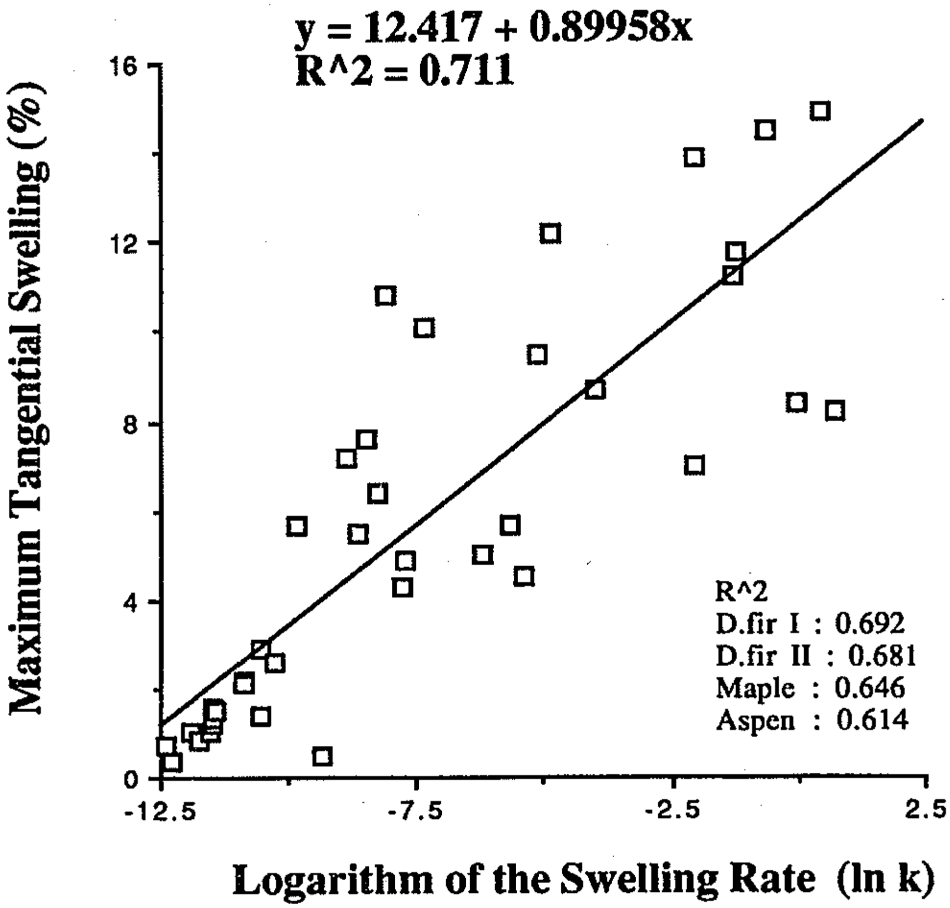

FIGURE 6-9. The maximum tangential swelling of spruce plotted against ln k.

6.2.3. Cellulose versus Wood Maximum Swelling

A physical classification of the organic liquids used in this experiment is given in Table 6-5. We divided the swelling liquids into five chemical classes with the classification based on three solvent properties (molar volume, hydrogen bonding parameter, and cohesive energy density). Robertson (1964) evaluated the swelling of cellulose in five similar chemical classes. His swelling results for cellulose are plotted in Figure 6-10. None of the liquids of the classes III, IV, 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 (Figures 6-11, 6-12). 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 wood maximum swelling indicate that the cellulose polymer is probably primarily responsible for the maximum wood swelling.

Previous workers (Nayer et al., 1949; Stamm, 1964) have suggested 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 bonding ability of the solvent and its swelling capability for wood clearly

TABLE 6-5

Chemical Classification of Organic Liquids

Class I.	Class II.	Class III.	Class IV.	Class V.
High CED[a]	Medium CED	High CED	Low CED	
Low Molar Volume	Low Molar Volume	Low Molar Volume	Low Molar Volume	Molar Volume
Hydrogen Bonds	Hydrogen Bonds	No Hydrogen Bonds	No Hydrogen Bonds	Greater than 100 cc
Water (H)[b]	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 & amines have a high hydrogen bonding parameter (Lieberman, 1962).

Note: Data from Robertson (1964)

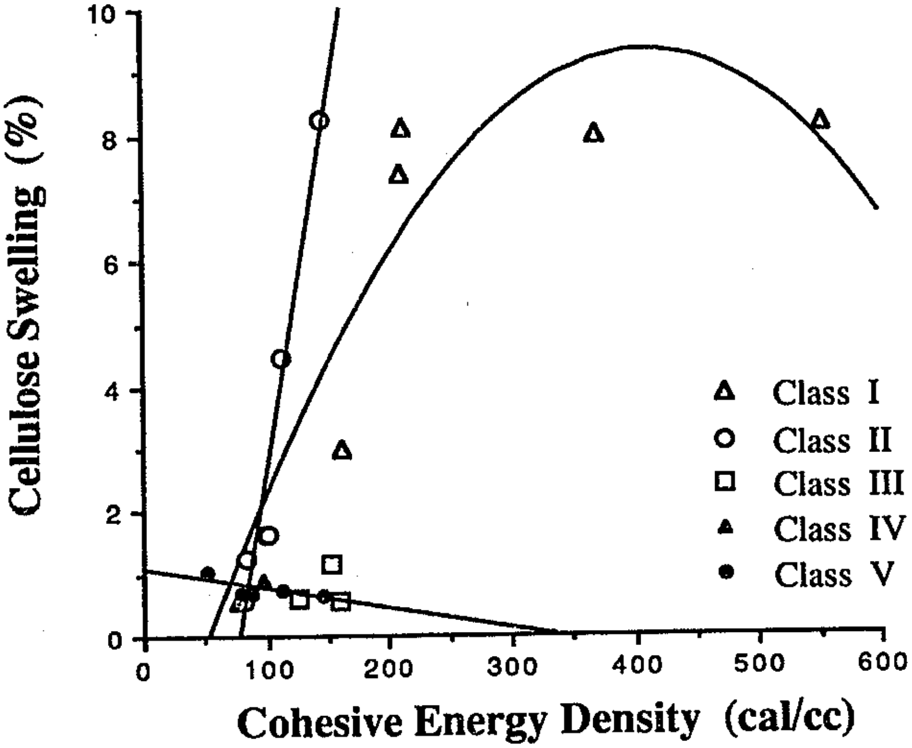

FIGURE 6-10. Cellulose swelling versus CED within various solvent classes.

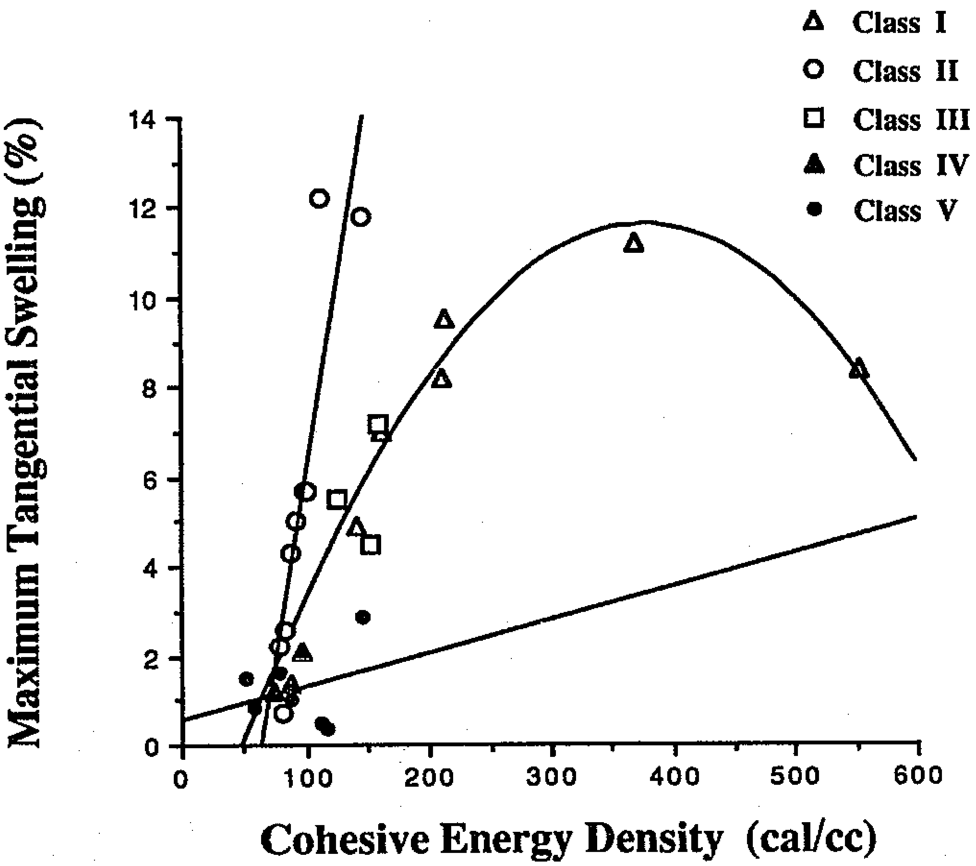

FIGURE 6-11. Sitka spruce swelling versus solvent CED within various solvent classes.

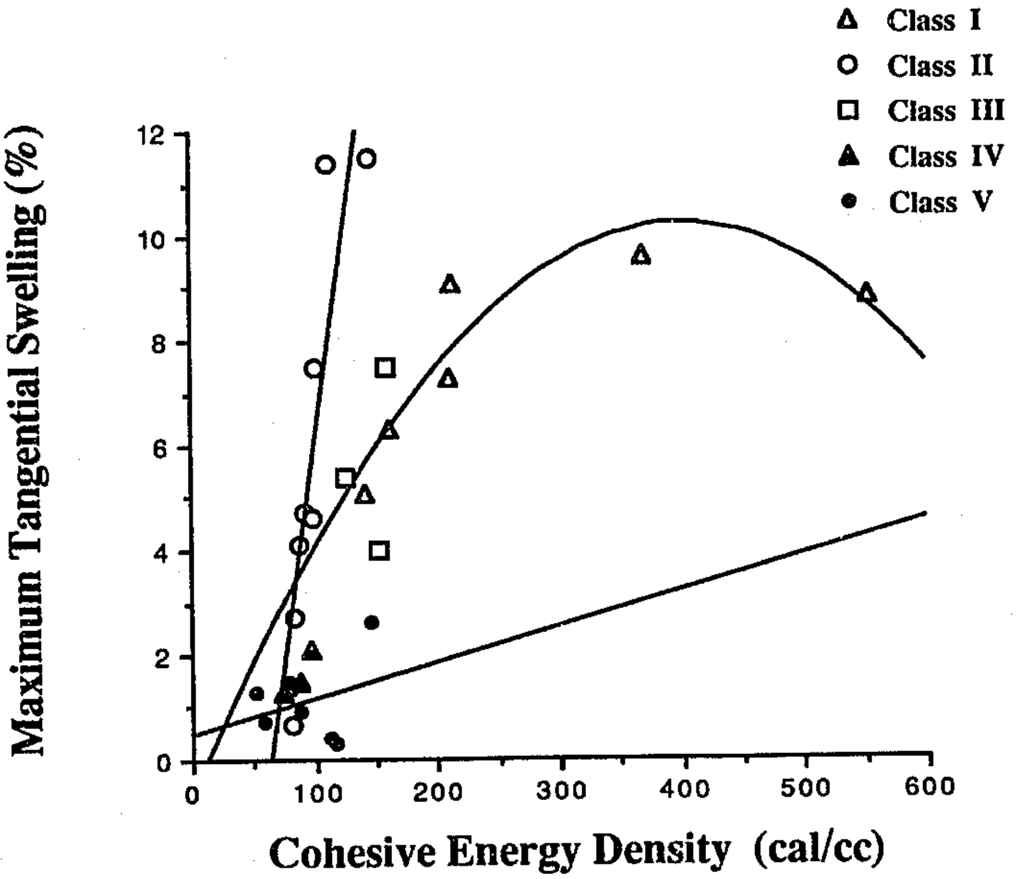

FIGURE 6-12. Douglas-fir I swelling versus solvent CED within various solvent classes.

suggests a 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 (HBP), would be expected to swell wood to the greatest extent. Indeed, Figure 6-13 clearly shows that solvents with a high HBP swelled wood more than those of a medium or low HBP. This is true for all wood species. Each column represents the average maximum swelling in each solvent class (high, medium, and low HBP) within the same wood species.

6.2.4. Activation Energy of Wood Swelling in Organic Liquids

Maximum swelling values and activation energies for wood swelling in the organic liquids are presented in Table 6-6. 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 experiment on wood swelling in water (Chapter 5.2.2). 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, 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 Ea. 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).

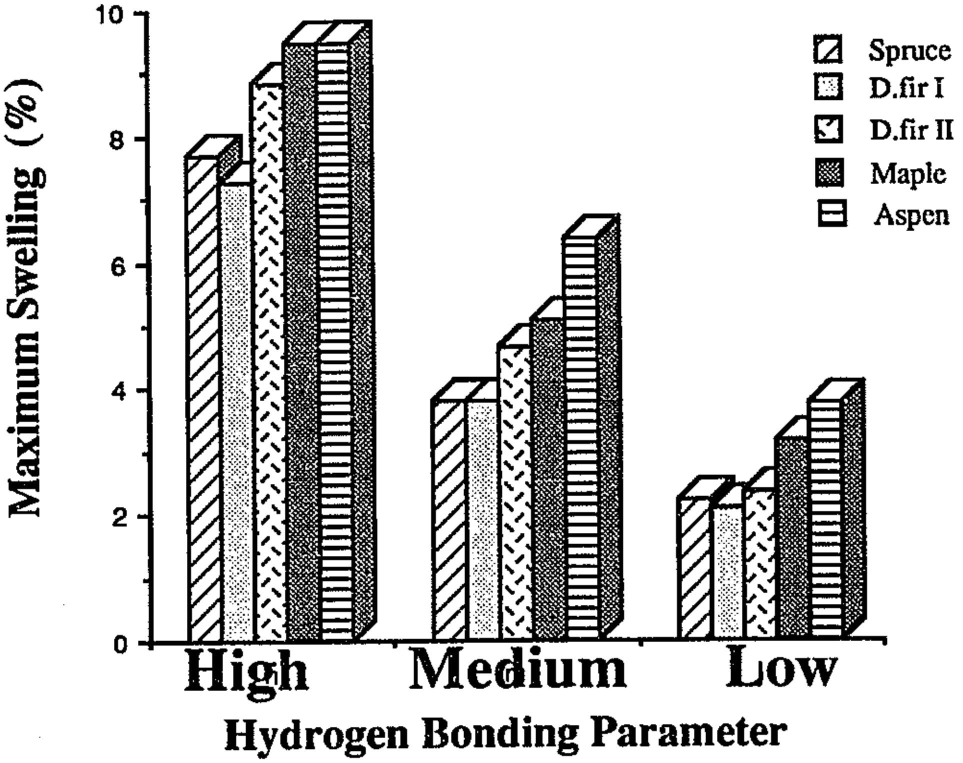

FIGURE 6-13. The effect of the solvent hydrogen bonding capability on the maximum tangential swelling of wood.

TABLE 6-6

Maximum Tangential Swelling Values and Activation Energies (E_a) for Wood Swelling in Various Organic Liquids

Swelling liquid	Maximum [a] Swelling (%)	Ea [b] (KJ/mol)	R^2 [c]	Maximum Swelling (%)	Ea (KJ/mol)	R^2
	Sitka Spruce			**Quaking Aspen**		
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
Ethylene dichloride	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
Carbon tetrachloride	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			**Sugar 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 (5 runs each).

[b] Ea is the average of two replicates except for water (5 runs).

[c] R^2 obtained from the Arrhenius plots (lnk vs. 1/T) (average of 2 runs).

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 Ea 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 Ea can be divided in two parts:

a. The major part of the measured Ea 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.

b. A part of the Ea 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 (Figure 6-14) 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 initial diffusion of 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

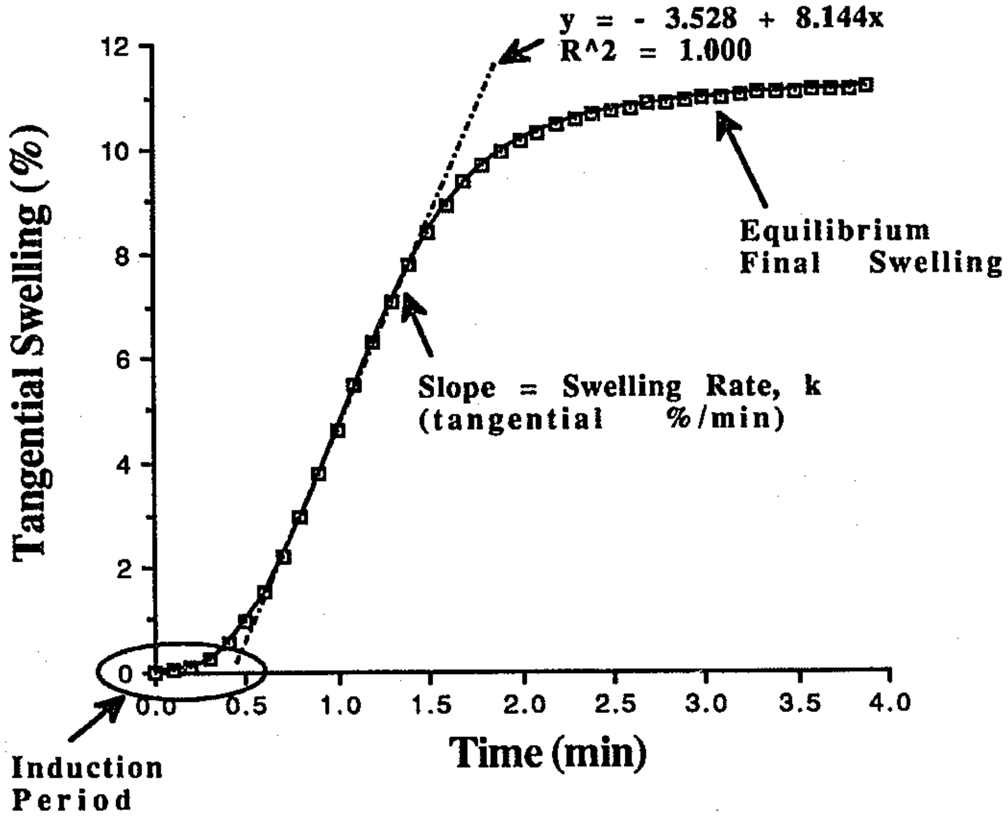

FIGURE 6-14. Schematic swelling profile of aspen in butylamine at 60° C.

(constant k) (Figure 6-14). 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 6-14, the initial portion of the schematic swelling profile of aspen in butylamine at 60° C is linear; the slope of which gives the swelling rate constant (k = 8.1 %/min).

Figure 6-15 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 (Ea) for aspen in butylamine was then calculated from an Arrhenius plot (Figure 6-16). 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 6-6).

The rate of wood swelling is mainly affected by both the magnitude of the Ea and the pre-exponent factor A (Eq. 4.2), 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 Ea 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

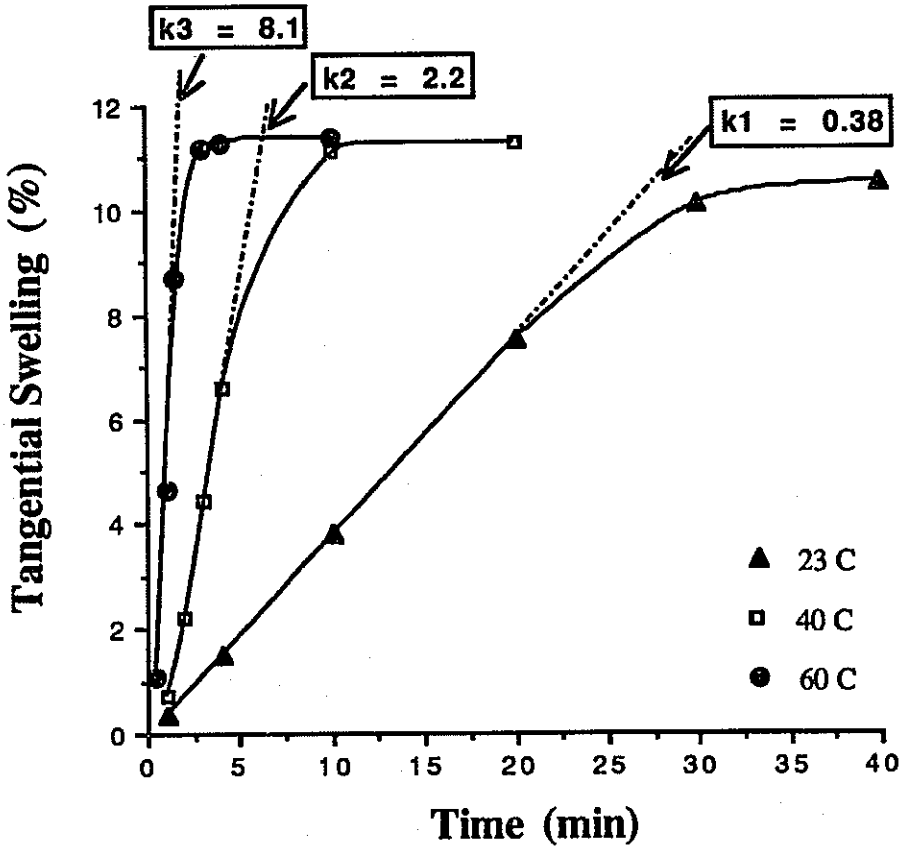

FIGURE 6-15. Swelling of aspen in butylamine at various temperatures.

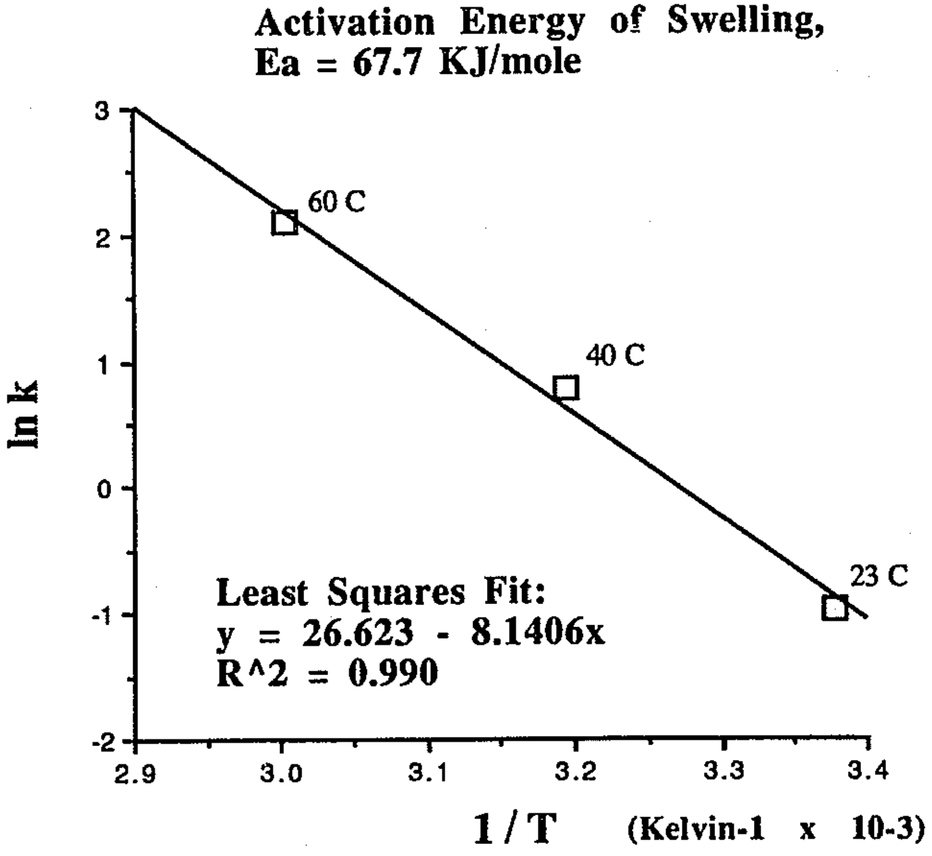

FIGURE 6-16. Arrhenius plot for aspen swelling in butylamine.

temperatures (80 to 100° C) and swelling reached an equilibrium state in a period of 5 to 10 minutes, while at room temperature (23° C), it took approximately three months to reach a maximum (Chapter 6.2.1). Similar 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 Ea of wood swelling and the solvent molecular weight (MW) (Figure 6-17). Consistent linear trends were also found to exist between Ea and molar volume (MV) (Figure 6-18). Very similar trends were found for the activation energies for wood swelling within a homologous series of alcohols (Figure 6-19). It is apparent that, in this case, the addition of a -CH_3 group causes a subsequent increase in the Ea. 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 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 6-6). It was additionally found that no correlations existed between wood swelling Ea and density of the wood species.

Table 6-7 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, liquids with a medium to low HBP seem to have a higher

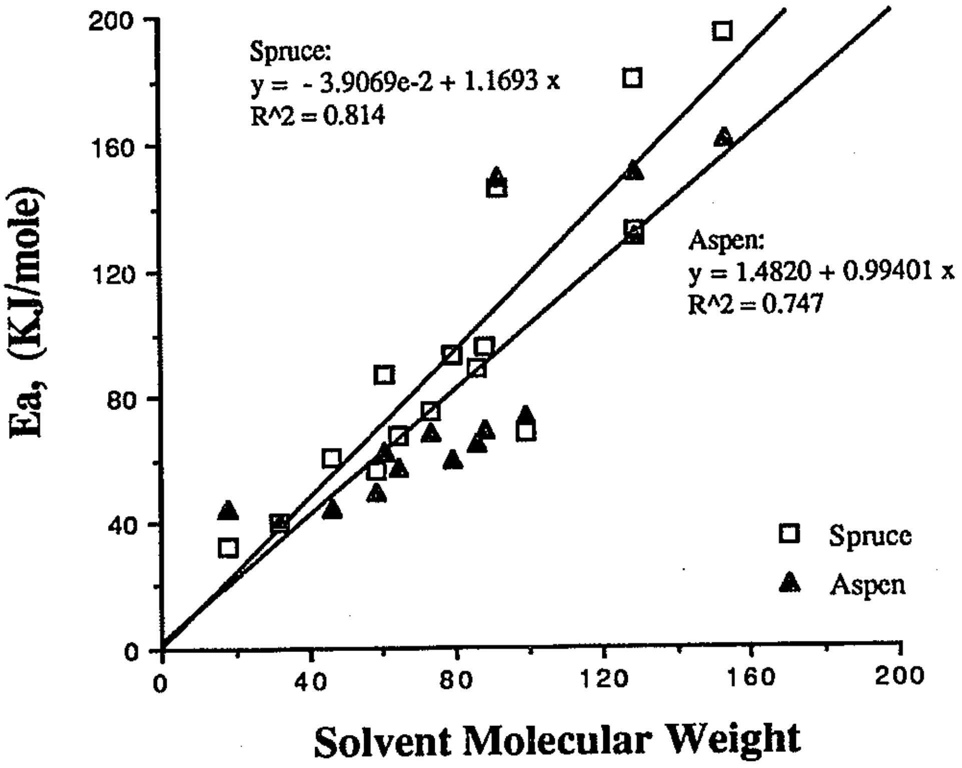

FIGURE 6-17. Activation energy of wood swelling, Ea, versus solvent molecular weight.

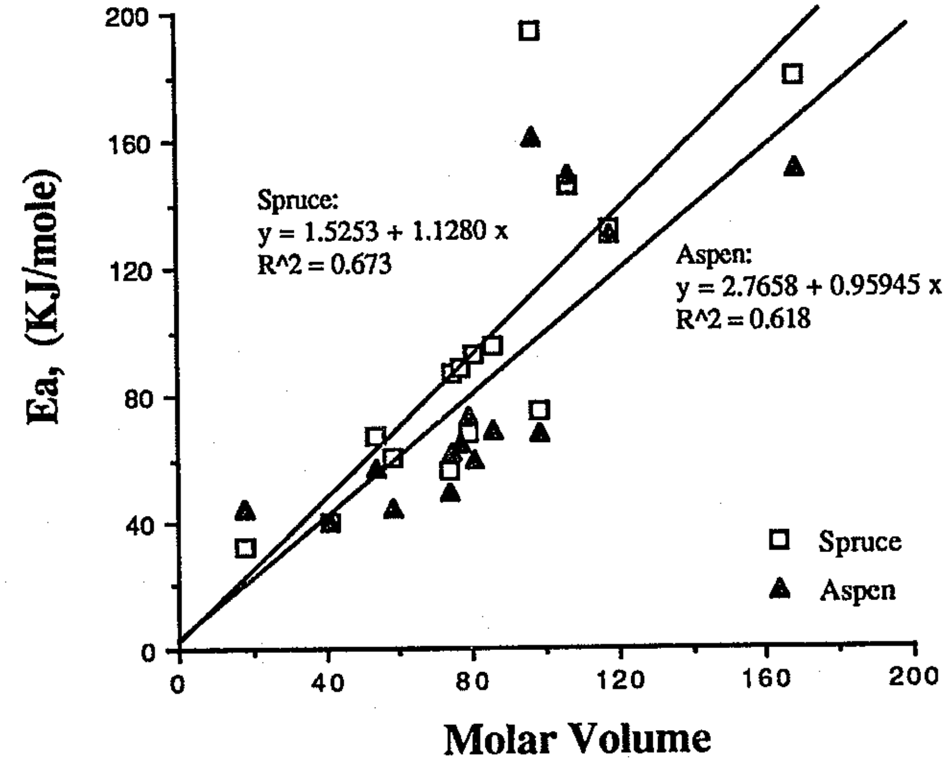

FIGURE 6-18. Activation energy of wood swelling, Ea, versus solvent molar volume.

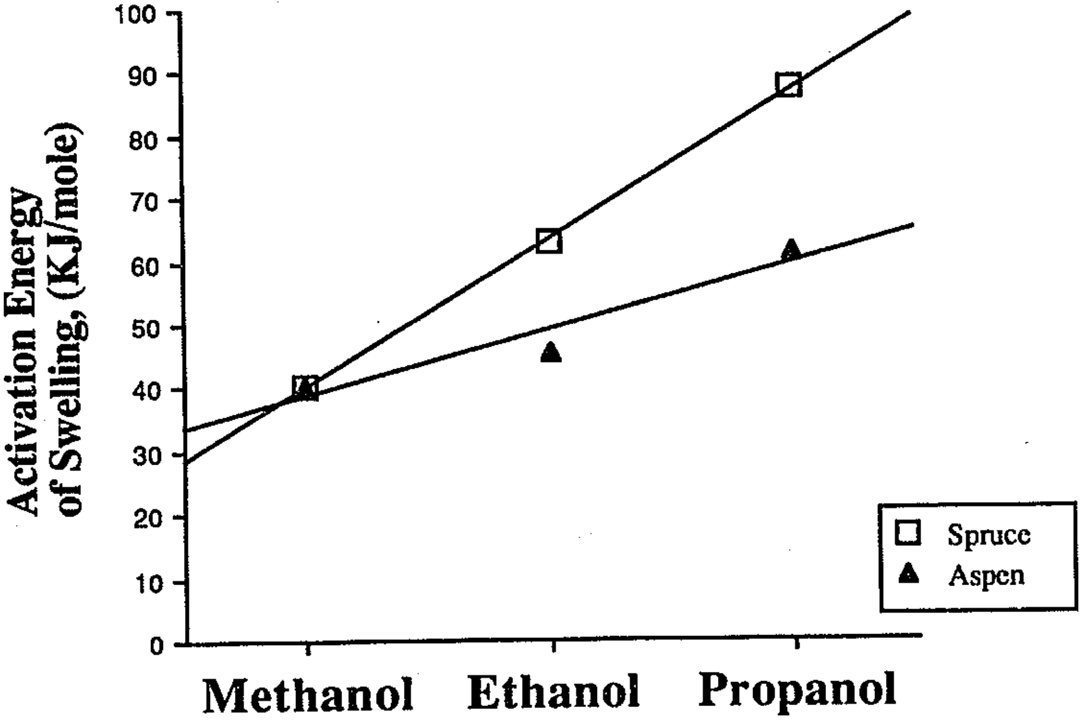

FIGURE 6-19. Activation energies for wood swelling in alcohols.

TABLE 6-7

Swelling Liquid Properties versus Ea of Wood Swelling

Liquids	HBP *	CED **	Ea (spruce) (KJ/mole)	Ea (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	59.6
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

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* Hydrogen bonding parameter (HBP) data from Lieberman (1962)

** Cohesive energy density (CED) data from Robertson (1964)

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 tend. 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 6-20 and 6-21. Each column represents the average Ea in each solvent class (low, medium, and high HBP or CED).

6.3. Summary

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.

The rate of wood swelling in organic liquids is clearly dependent upon the temperature and very closely obeys the classical Arrhenius equation (Eq. 4.2). 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

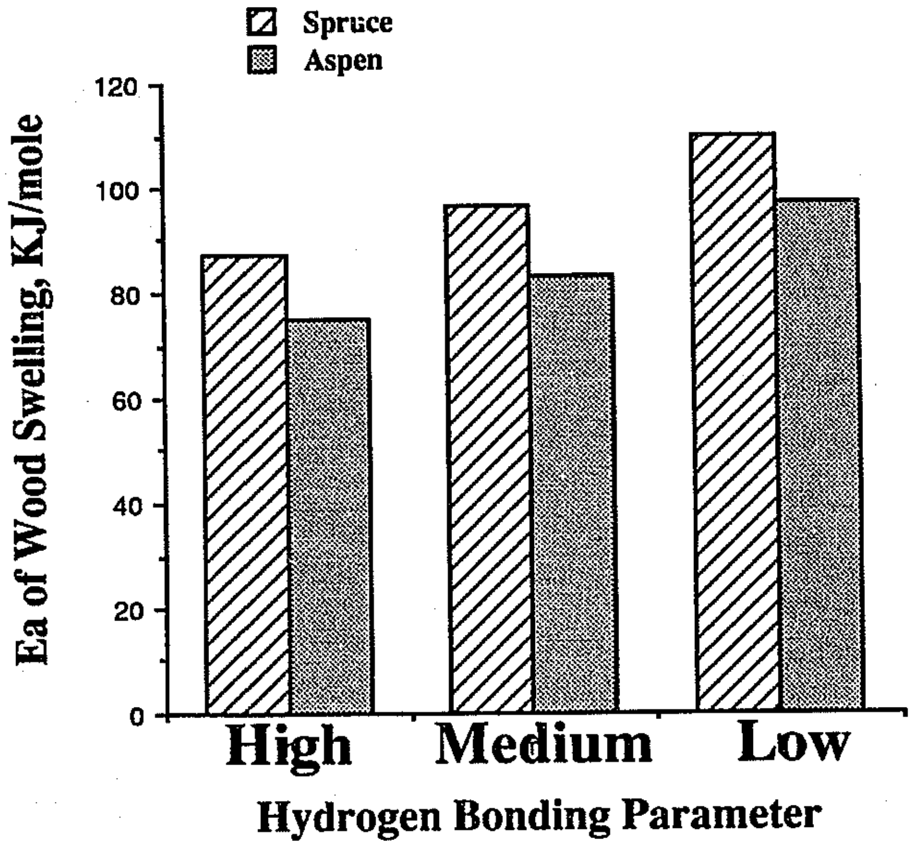

FIGURE 6-20. The effect of the solvent hydrogen bonding parameter on the activation energy of wood swelling.

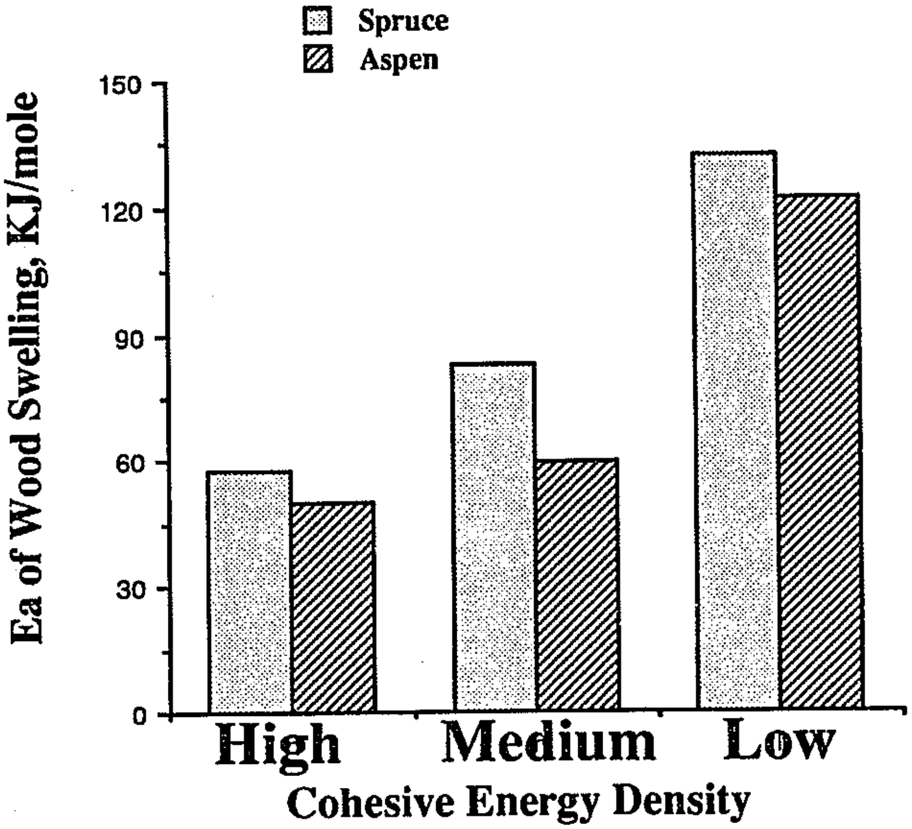

FIGURE 6-21. The effect of the solvent cohesive energy density on the activation energy of wood swelling.

raising the temperature. Data from the variation of wood swelling rate with temperature were used to derive activation energies (Ea) for the wood swelling process in fifteen various organic liquids. Wood swelling Ea was linearly correlated with the molecular weight and the molar volume of the swelling liquid.

CHAPTER SEVEN

EFFECT OF EXTRACTIVES ON WOOD SWELLING

7.1. Introduction

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 in 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. In general, removal of extractives has been found to enhance swelling significantly (Stamm, 1935; Nayer, 1948; Stamm, 1964), especially in species which have a large percentage of extractives (ie. pines and other conifers).

7.2. Results and Discussion

7.2.1. Swelling in Water

It has been shown that the extractives and their removal can considerably influence the rate and percentage swelling of wood (Nayer, 1948; Stamm, 1964; Boiciuc and Petrician, 1970). Indeed, as shown in Table 7-1 and in Figures 7-1 and 7-2, the rate of swelling of wood considerably increased after removal of extractives and the maximum equilibrium swelling generally increased on the average by 5 - 10 % (Figure 7-3). Additionally, it was found that removal of extractives from wood caused a large decrease in the activation energy (Table 7-1), that is, the swelling of extracted wood was much more facile. Since the activation energy, Ea, mainly represents the energy required to break the wood hydrogen bonds, it appears that the removal of the extractives, even with mild procedures, disrupts the internal structure of the cell wall, decreasing the network of secondary bonds, such that the cell wall structure is in a more loosely bonded state. This further suggests that either the extractives serve a role in the cell wall structure or the solvent used for removal is itself disruptive to the cell wall; probably both effects are operative. This interpretation is consistent with the observation that cell wall sugars are also removed in the extraction procedure (Table 4-8). However, a part of this energy is contributed from the energy required to pull a solvent molecule momentarily away from the bulk of the liquid (West, 1988).

7.2.2. Swelling in Organic Liquids

Table 7-2 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

TABLE 7-1

Rate of Swelling, Maximum Tangential Swelling and Activation Energy of Swelling of Unextracted and Extracted Wood in Water

	SPRUCE		D.FIR I		D.FIR II		MAPLE		ASPEN	
	UN*	EX.	UN.	EX.	UN.	EX.	UN.	EX.	UN.	EX.
Swelling Rate, k, (%/min) Temperature, (Celsius)										
23	1.3	7.2	0.3	0.16	0.7	0.28	0.3	0.9	0.8	0.8
40	3.3	14.9	0.9	1.2	1.4	0.8	1.1	4.0	2.1	2.6
60	6.5	25.8	1.8	1.4	3.1	1.5	3.6	7.1	5.9	5.4
80	10.8	32.4	4.7	3.2	4.2	3.7	6.6	16.7	14.4	8.7
100	14.8	36.2	6.9	3.4	5.8	5.5	7.6	20.7	20.4	13.8
Maximum Tangential Swelling, (%)										
23	6.5	7.4	7.6	9.0	8.7	9.7	10.0	10.7	9.1	9.5
40	6.9	7.5	7.7	9.1	8.8	9.7	10.8	11.6	8.9	9.4
60	6.9	7.7	7.7	9.1	9.0	9.8	11.5	11.4	9.4	9.5
80	7.2	7.7	8.0	9.1	9.1	9.8	11.5	11.2	9.6	9.5
100	7.3	7.7	8.1	9.2	9.3	9.9	12.3	11.3	10.1	10.0
Activation Energy, Ea, (KJ/mole)	32.2	23.3	38.9	41.5	33.0	35.4	47.6	42.3	44.7	36.9

* UN. : Unextracted wood; EX. : Extracted wood

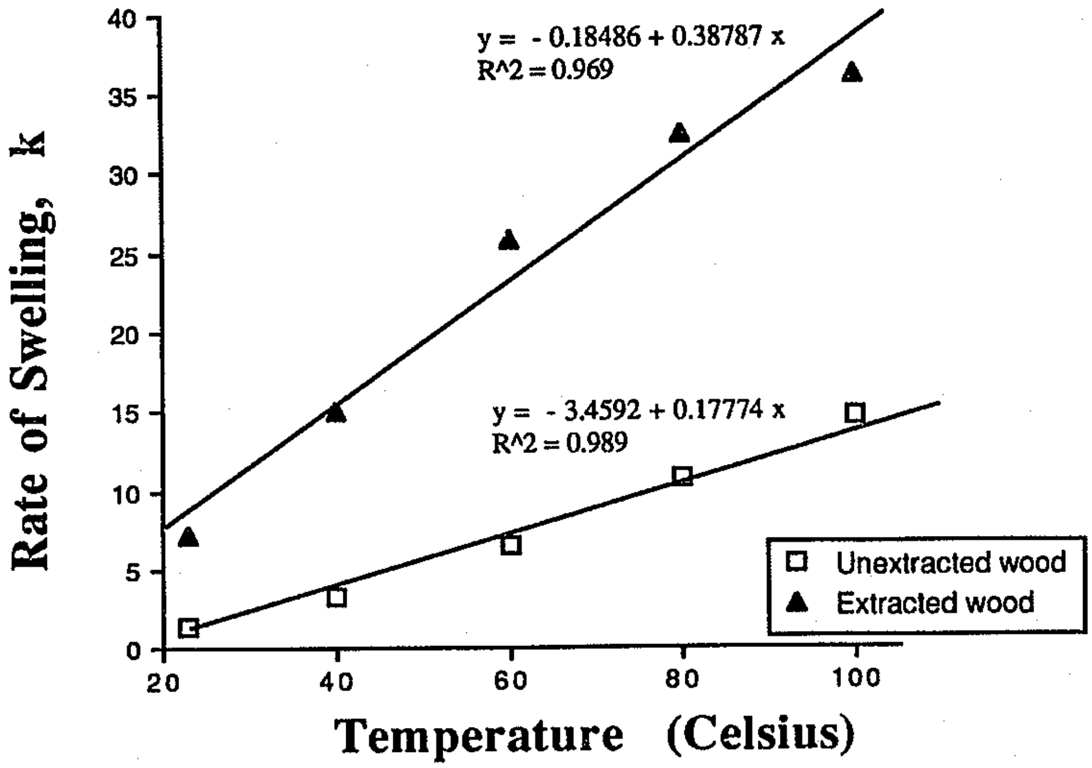

FIGURE 7-1. Swelling rate versus temperature for sitka spruce in water for unextracted and extracted wood.

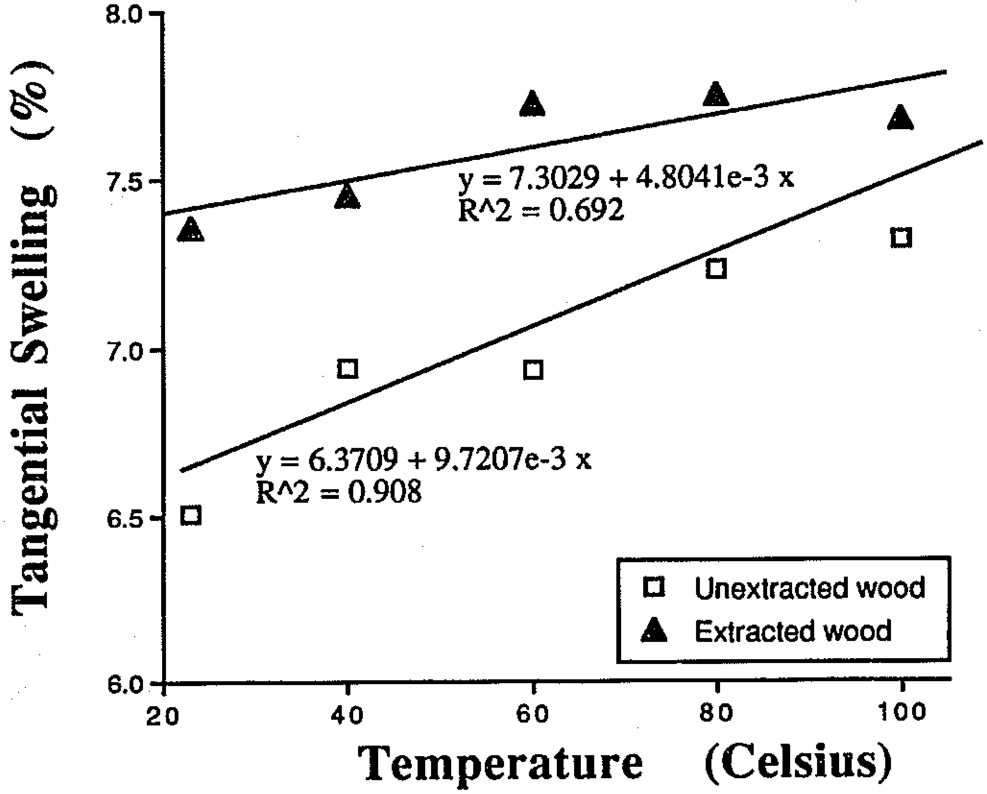

FIGURE 7-2. Maximum tangential swelling versus temperature for sitka spruce in water for unextracted and extracted wood.

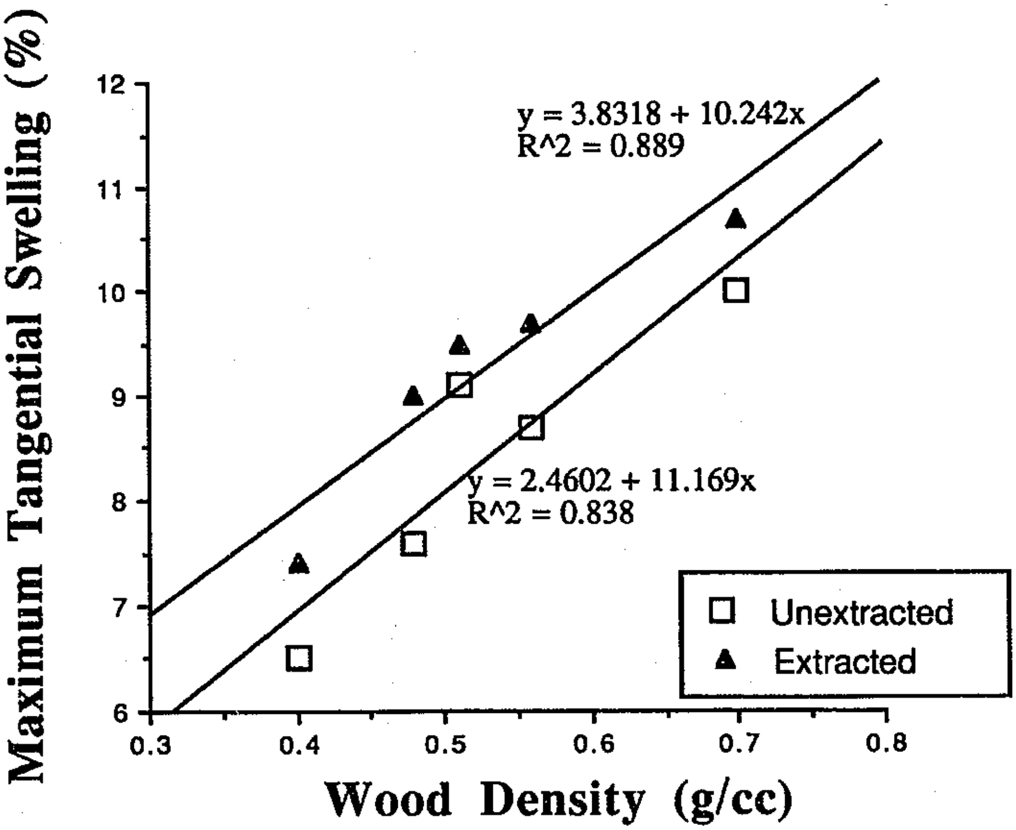

FIGURE 7-3. Maximum swelling of unextracted versus extracted wood in water at room temperature.

TABLE 7-2 (continued)

Maximum Tangential Swelling of Unextracted and Extracted Wood in Various Organic Liquids

	- Sitka Spruce -				- Sugar Maple -			
	Unextracted		Extracted		Unextracted		Extracted	
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)
Chroroform	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)

Note: Maximum tangential swelling values are the average of two replicates.

TABLE 7-2

Maximum Tangential Swelling of Unextracted and Extracted Wood in Various Organic Liquids

	- Sitka Spruce -				- Sugar Maple -			
	Unextracted		Extracted		Unextracted		Extracted	
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 (96%)	11.4	(0.3)	12.6	(0.3)	19.3	(0.5)	19.9	(0.5)
Acetic	5.6	(0.2)	5.7	(0.2)	9.4	(0.3)	11.4	(0.2)
Propionic	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)

Note: Maximum tangential swelling values are the average of 2 replicates.

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 7-3 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 (Figures 7-4, 7-5, 7-6, 7-7). 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,

(4) probable increase in the size of the microscopic capillaries during the process of extraction.

Wood extracts were analyzed by high pressure liquid chromatography (HPLC) which showed that there was a significant quantity of sugars were removed in the extraction procedure (Table 4-8). 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 7-4, 7-5, 7-6, and 7-7 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.

TABLE 7-3

Swelling Rates of Unextracted and Extracted Wood
in Various Organic Liquids (tangential % per min)

	- Sitka Spruce -		- Sugar Maple -	
Liquids	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	4.4e-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

Note: Each swelling rate is the average of two replicates.

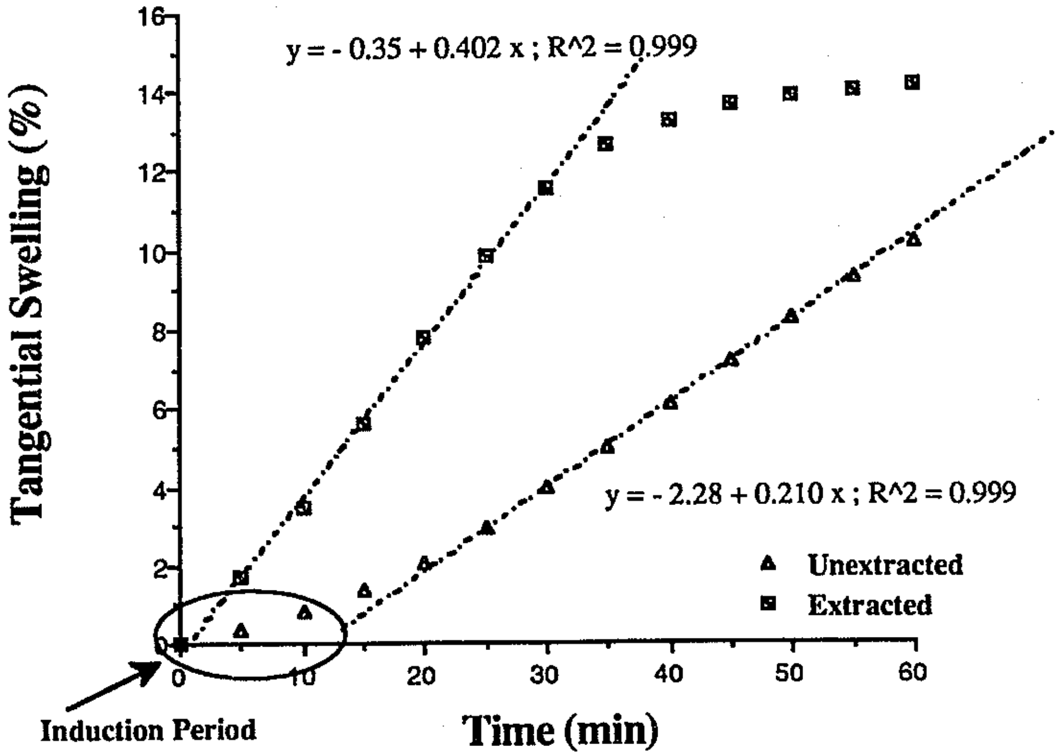

FIGURE 7-4. Initial linear swelling (maple in DMF at 23° C. Swelling rate k = Slope (tangential % per minute).

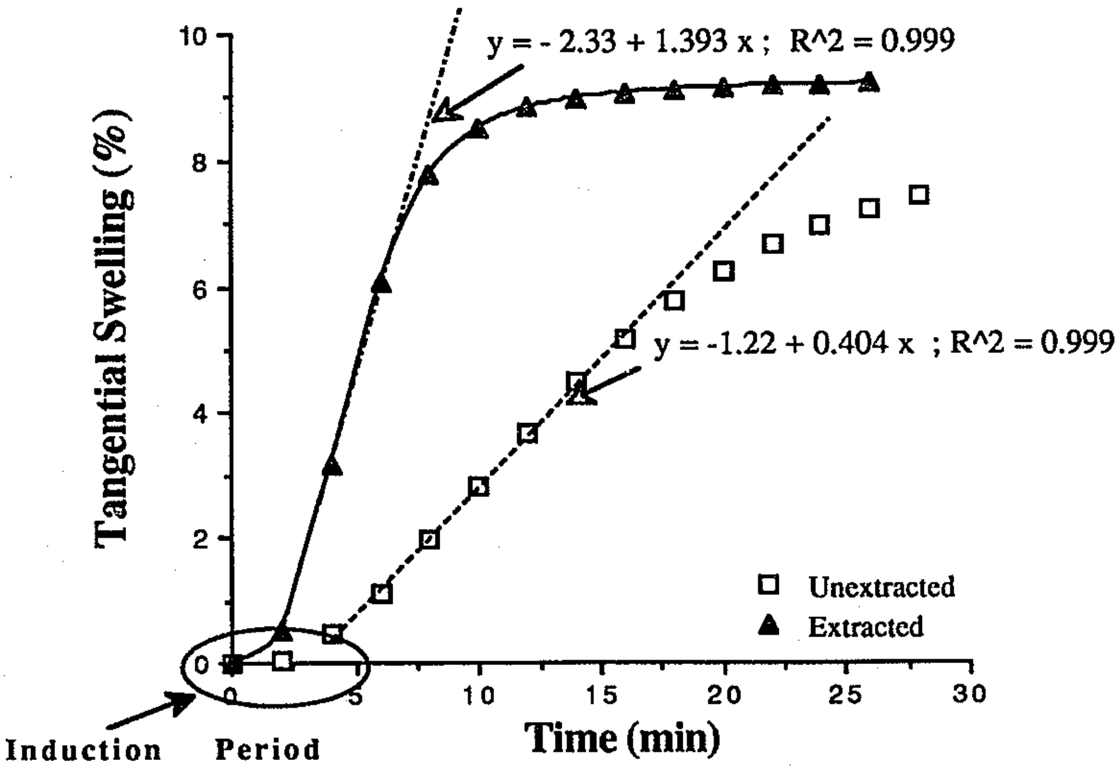

FIGURE 7-5. Swelling of unextracted and extracted spruce wood in butylamine at 23° C.

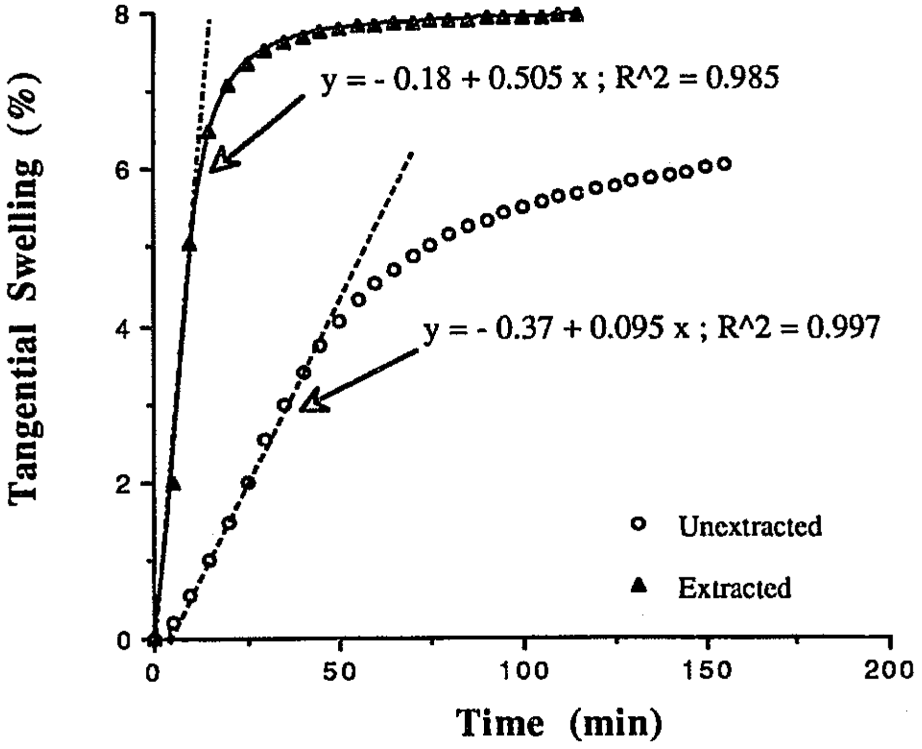

FIGURE 7-6. Swelling of unextracted and extracted maple wood in acetone at 23° C.

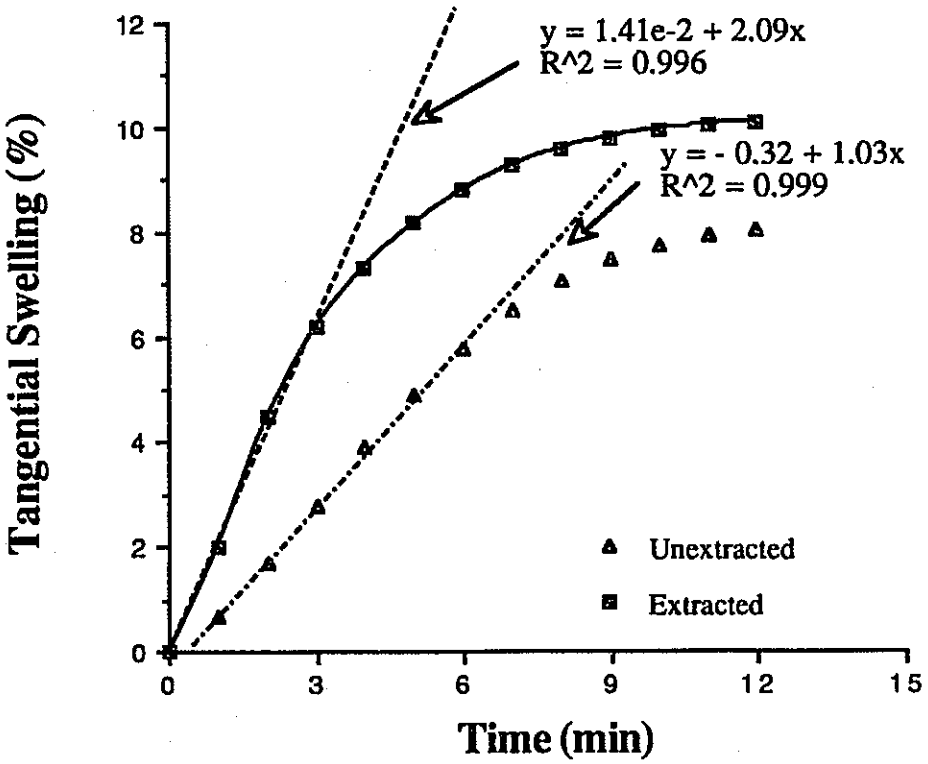

FIGURE 7-7. Swelling of unextracted and extracted maple wood in methanol at 23° C.

Extractives also seemed to affect the Ea of wood swelling. Strong linear correlations existed between the wood swelling Ea and the content of extractives in the wood species as shown for the wood swelling in acetone and butylamine (Figure 7-8). West (1988) found an Ea of 48 KJ/mole for the Scots pine swelling in acetone (Scots pine extractives' content is approximately 3.2 % (Fengel et al., 1984)). This Ea value is in a very good agreement with our results (47 KJ/mole) (Figure 7-8; Eq. 1). Similar trends were found for the wood swelling in water. However, no correlation was found between Ea 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 generally caused a decrease in the wood swelling Ea.

7.3. Summary

It was ascertained once again that removal of extractives caused an increase in the maximum equilibrium swelling of wood in water. It was also found that removal of extractives caused a large decrease in the swelling activation energy, Ea, for spruce, maple, and aspen (wood swelling in water). In addition, removal of extractives from wood caused a significant increase in the maximum tangential swelling of wood in an extensive series of organic liquids. There was also a notable increase in the wood swelling rate, that is, the swelling of extracted wood took place much faster than that of unextracted wood (spruce and maple). Also, extractives adversely influenced the Ea of wood swelling in certain organic solvents (butylamine, acetone, and water).

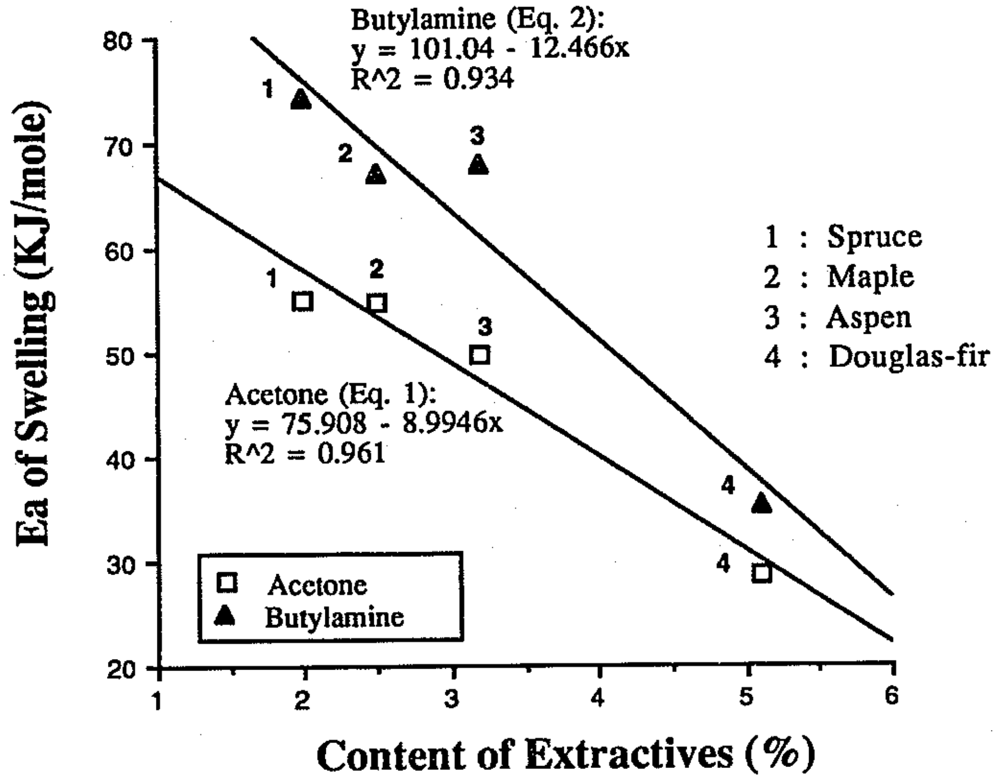

FIGURE 7-8. Effect of extractives on Ea of wood swelling in acetone and butylamine.

CHAPTER EIGHT

WETTING OF WOOD

8.1. Results and Discussion

Advancing contact angles, average cosines of θ , and works of adhesion of wood with water, methylene iodide, formamide and ethylene glycol are presented in Table 8-1. Water contact angles varied from 60° - 74°. Spruce and maple exhibited an average contact angle with water of 60.4 and 62.2 degrees, respectively. Douglas-fir had the largest advancing contact angle (73.5°). The low wettability of Douglas-fir is probably related to extractives and will be discussed later. Our results are in the same range as those reported by Kalnins (1993) for the wetting of western red-cedar with water (77°) and Banks and Voulgaridis (1980) (tilting plate method) for the water wetting of beech (70°) and Scots pine (80°). The work of adhesion, W_A, was also evaluated for all wood species with the probe liquids (Table 8-1). In general, spruce exhibited the highest work of adhesion while Douglas-fir had the lowest W_A (except in formamide). Douglas-fir had a maximum work of adhesion, W_A max, with water of about 104.5 dynes/cm, a result which is in an agreement with Marian's (1963) (118 dynes/cm) and Herczeg's work (1965) (122.5 dynes/cm).

Figure 8-1 shows the acid-base work of adhesion, W_A^{ab}, calculated for all wood species. It is obvious that all wood surfaces have a very strong acidic character because the strongest interactions occured with formamide (basic probe) while much weaker interactions occured with ethylene glycol (acidic probe). Similar results were reported

TABLE 8-1

Wetting Parameters (϶, $\cos\theta$, W_A) of Wood with Probe Liquids

	Water			Diiodomethane			Formamide			Ethylene glycol		
Species	θ	$\cos\theta$	W_A [a]	θ	$\cos\theta$	W_A	θ	$\cos\theta$	W_A	θ	$\cos\theta$	W_A
Spruce	60.4	0.486	108.5	13.4	0.953	99.2	27.8	0.882	109.7	0.8	0.999	96.6
Douglas-fir	73.5	0.280	93.4	41.8	0.739	88.3	36.8	0.796	104.7	42.4	0.731	83.6
Maple	62.2	0.464	106.9	32.3	0.841	93.5	37.9	0.786	104.1	10.6	0.975	95.4
Aspen	68.2	0.369	99.9	28.1	0.877	95.4	48.9	0.653	96.4	40.0	0.763	85.2

[a] W_A, (dynes/cm)

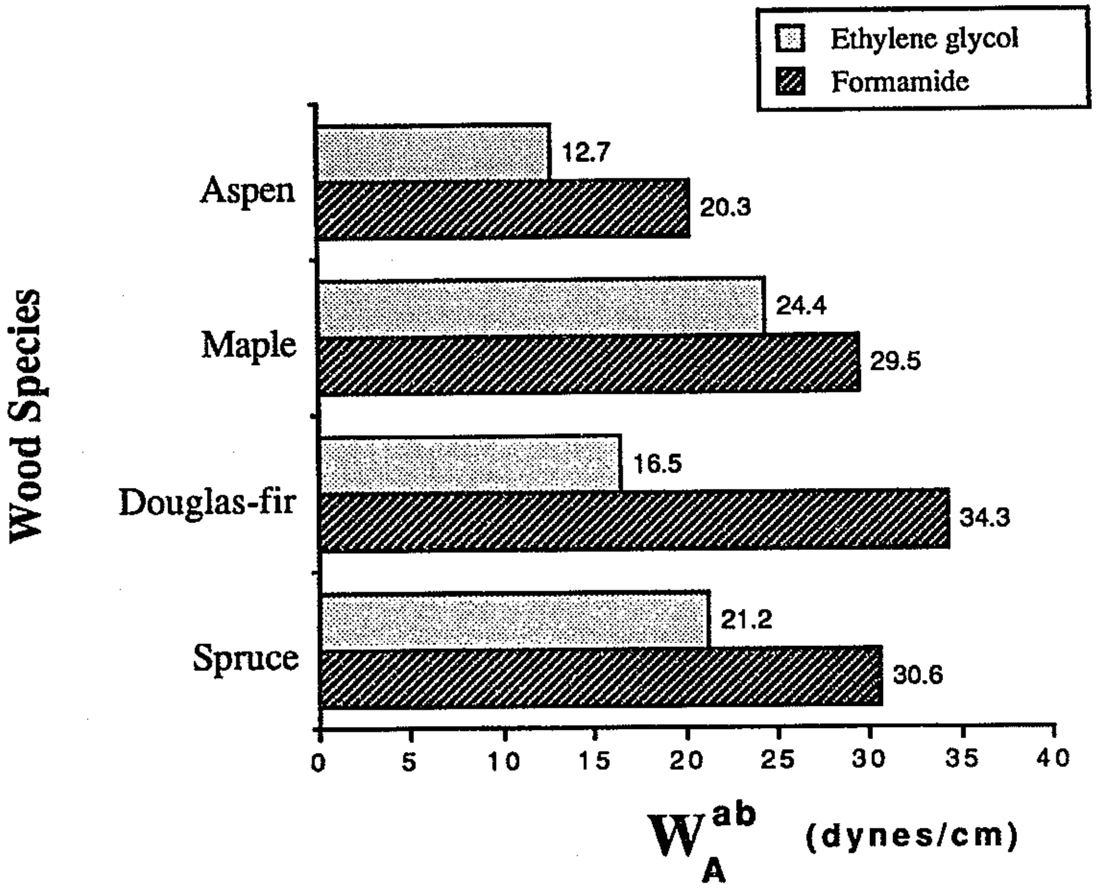

FIGURE 8-1. Acid-base work of adhesion of wood.

by Fernandez (1993) for the acid-base work of adhesion of various pulps (strong acidic character of kraft and sulfite pulp fibers). This behavior was explained by the presence of acidic type functional groups (i.e., carboxyl) on the fiber surface.

Table 8-2 presents the dispersive and polar surface free energies of the four wood species obtained using Wu's equations (Wu, 1971) as previously described. Standard deviations are also shown in the parentheses. In general, wood shows a very high dispersive surface free energy component, γ_s^d. Approximately seventy five to eighty percent (on the average) of the overall wood surface energy was attributed to the dispersion forces. This is consistent with Nguyen and Johns (1979) conclusions that "the dispersion forces on the surface of wood (Douglas-fir) are predominant in surface interactions". Young et al. (1982) have also shown that wood surfaces are hydrophobic based on ESCA analyses. The total surface energy of wood varied from 48.0 dynes/cm for Douglas-fir to 61.5 dynes/cm for sitka spruce.

Marian (1963) has reported a total surface tension of wood of around 50 ergs/cm^2. Similarly, Nguyen and Johns (1979) found a total surface free energy for Douglas-fir of about 48.0 dynes/cm; however, they reported a polarity (γ_s^p / γ_s) for Douglas-fir of 40 %, which is higher than our result (24 %). Herczeg (1965) reported a total γ_s for Douglas-fir wood of about 58 dynes/cm. The γ_s values found in this work are also in the range of values reported for wood previously (49.5 dynes/cm for birch) (Kalnins, 1987). The polarity of the wood surface was found to be in the range of 24.0 to 29.0 % in this study (Table 8-2). Douglas-fir exhibited the lowest polarity values (24.0 %) on the average. Polarity is independent of the temperature but it should be noted that the polar component of the overall surface free energy is considered to be an inadequate measure of polarity or hydrophilicity of the surface.

Table 8-3 shows the advancing specific wettabilities and calculated contact angles of two wood species (spruce, maple) in various wetting liquids. In general, spruce

TABLE 8-2

Dispersive and Polar Components of Surface Free Energies of Wood [1]

Species	γ_s^d (SD) [2] (dynes/cm)	γ_s^p (SD) (dynes/cm)	γ_s (dynes/cm)	Polarity [3], γ_s^p/γ_s
Spruce	45.0 (2.3)	16.5 (4.5)	61.5	0.268
Douglas-fir	36.2 (3.4)	11.8 (3.5)	48.0	0.246
Maple	40.2 (5.8)	16.4 (1.7)	56.6	0.290
Aspen	41.8 (2.0)	13.2 (2.8)	55.0	0.240

[1] Calculated with Wu's simultaneous equations (1971)
[2] SD: Standard deviation
[3] Polarity is independent of temperature

TABLE 8-3

Wetting Parameters of Spruce and Maple Wood in Various Organic Liquids

	Sitka Spruce			Sugar Maple		
Wetting liquid	W_S [a] dyn/cm	cosθ	θ (degr)	W_S dyn/cm	cosθ	θ (degr)
Water	35.5	0.486	60.4	33.9	0.464	62.2
Formamide	51.4	0.882	27.8	45.8	0.786	37.9
Ethylene glycol	48.2	0.999	0.8	47.1	0.975	10.6
Methanol	29.2	1.29	0	27.1	1.20	0
Ethanol	26.6	1.17	0	26.2	1.15	0
Propanol	28.1	1.18	0	26.1	1.10	0
Dimethylformamide	39.4	1.07	0	40.8	1.11	0
Pyridine	34.2	0.90	24.5	33.8	0.89	26.0
Acetone	28.0	1.18	0	27.0	1.14	0
Methylethyl ketone	32.2	1.31	0	28.5	1.16	0
Methylacetate	32.2	1.31	0	29.3	1.19	0
Ethylacetate	30.8	1.29	0	30.8	1.29	0
Propylacetate	31.1	1.28	0	29.4	1.21	0
Nitromethane	35.3	0.96	15.3	31.3	0.85	31.9
Furfural	50.4	1.16	0	46.1	1.06	0
Chloroform	35.8	1.32	0	34.5	1.27	0
Ethylene dichloride	40.2	1.72	0	37.9	1.62	0
Carbon tetrachloride	35.0	1.30	0	33.7	1.25	0
Benzaldehyde	45.6	1.14	0	45.6	1.14	0
Nitrobenzene	36.0	0.82	35.3	40.8	0.93	20.3
Toluene	34.8	1.22	0	31.1	1.09	0
Benzyl alcohol	43.3	1.11	0	44.9	1.15	0
Quinoline (98%)	50.3	1.00	1.0	49.3	0.98	11.9
Dimethylsulfoxide	53.1	1.22	0	45.7	1.05	0
Formic acid (96%)	48.1	1.01	0	47.6	1.00	0
Acetic acid	35.9	1.29	0	32.2	1.16	0
Propionic acid	32.3	1.21	0	32.8	1.23	0
Diethylamine	26.9	1.64	0	24.6	1.50	0
Butylamine	28.4	1.44	0	27.8	1.41	0
Methylene iodide	48.4	0.953	13.4	42.7	0.841	32.3

[a] W_S = Advancing specific wettability

showed higher wettabilities than maple (except with nitrobenzene, benzyl alcohol, propionic acid, and DMF). Most of the liquids completely wetted both species forming zero advancing contact angles (except with water, formamide, ethylene glycol, methylene iodide, pyridine, nitromethane, nitrobenzene, and quinoline). Also, in most cases, receding contact angles were zero or near zero for all wood species. Overall, the highest specific wettabilities, W_S, for spruce were with DMSO, formamide, furfural, quinoline, methylene iodide, ethylene glycol, and formic acid (in descending order), and for maple with quinoline, formic acid, ethylene glycol, furfural, formamide, DMSO, benzaldehyde, and benzyl alcohol (in descending order). The lowest Ws were obtained with diethylamine, propanol, ethanol, methanol, and butylamine (for both wood species).

The wood wettability, in general, reflects the composite chemical and morphological character of the wood. The type of the wood species seems to affect differently the wetting behavior of wood. High water wettability can be caused by various hydrophilic components on the wood surface such as hemicelluloses. However, the presence of extractives at the wood surface can also influence the wettability depending upon the wood species (Young, 1976). According to Kajita and Skaar (1992), the extractives play a significant role affecting the water wettability of wood by two effects. One is direct on the wettability of the true surface and the other effect is the blockage by extractives of the openings between the cells, thus preventing penetration of a droplet below the surface of the wood. Also, Nguyen et al. (1979) attributed the low relatively wettability of Douglas-fir wood to nonpolar extractives. It was indeed found that the specific wettability of wood (four species) in water was inversely correlated with the percentage of extractives within the wood species (Figure 8-2). The higher the extractives content, the lower the wood wettability in water. Other characteristics, as suggested by Young (1976), that can influence wettability include the degree of

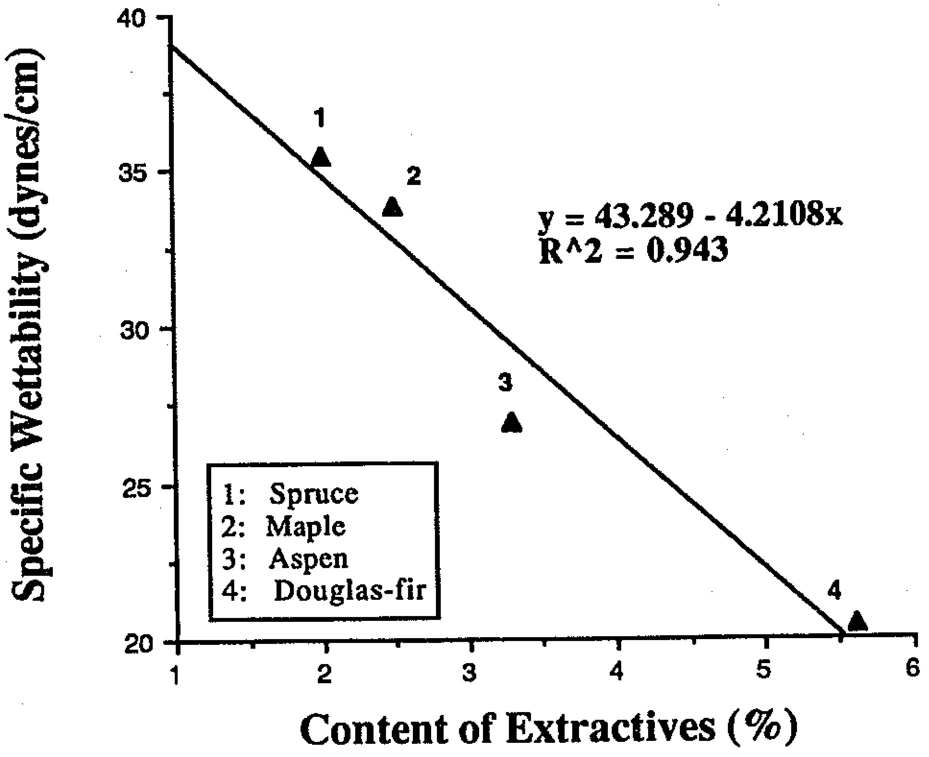

FIGURE 8-2. Specific water wettability as a function of content of extractives for four wood species.

polymerization of some surface polymers, the degree of surface crystallinity, and the presence of monolayers at the wood surface (e.g. water).

Figures 8-3 and 8-4 show that a inverse linear relationship exists between the cosine of θ and the liquid surface tension for the thirty various wetting liquids (Zisman plots), consistent with the literature. The critical surface tensions of spruce and maple were found to be 45.0 dynes/cm and 42.0 dynes/cm, respectively. Critical surface tension values for these two wood species were slightly smaller (14 - 16 dynes/cm) than their total surface free energies. Herczeg (1965) found that the surface free energy of Douglas-fir was 61.0 to 58.2 dynes/cm (springwood and summerwood, respectively), which were about 11.0 to 14.0 units higher than γ_c. Nguyen et al. (1979) reported a γ_c of 52.8 dynes/cm for unextracted Douglas-fir wood. Jacob and Berg (1993) found critical surface tension values of 32.0, 35.0, and 37.0 dynes/cm for softwood bleached kraft, hardwood bleached kraft, and chemithermomechanical pulp fibers, respectively. Also, Luner et al. (1969) found critical surface tensions of 36.0 to 49.0 erg/cm^2 for cellulose and 33.0 to 36.0 erg/cm^2 for hemicelluloses. As previously discussed, differences are probably due to the variable effects of the physical and chemical state of the surfaces.

An attempt to correlate wood wettability and tangential swelling of wood (Chapter 6.2.1) in various organic solvents was unsuccessful (Figure 8-5). The strong acidic character of the wood surface is a significant factor in the initial process of wetting and swelling but the ultimate swelling of wood is apparently independent of specific wettability.

8.2. Summary

The wettability of wood in thirty various organic liquids was determined using the Wilhelmy technique. Wood surfaces have a strong acidic character since the greatest interactions for all four wood species occurred with the basic probe (formamide), while

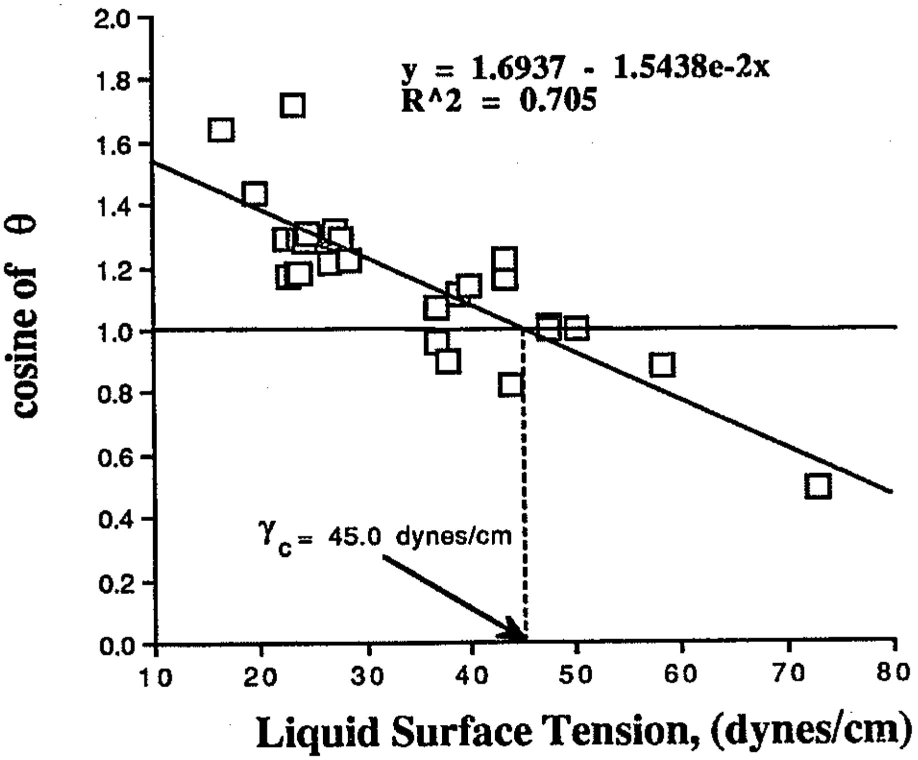

FIGURE 8-3. Determination of critical surface tension of sitka spruce wood.

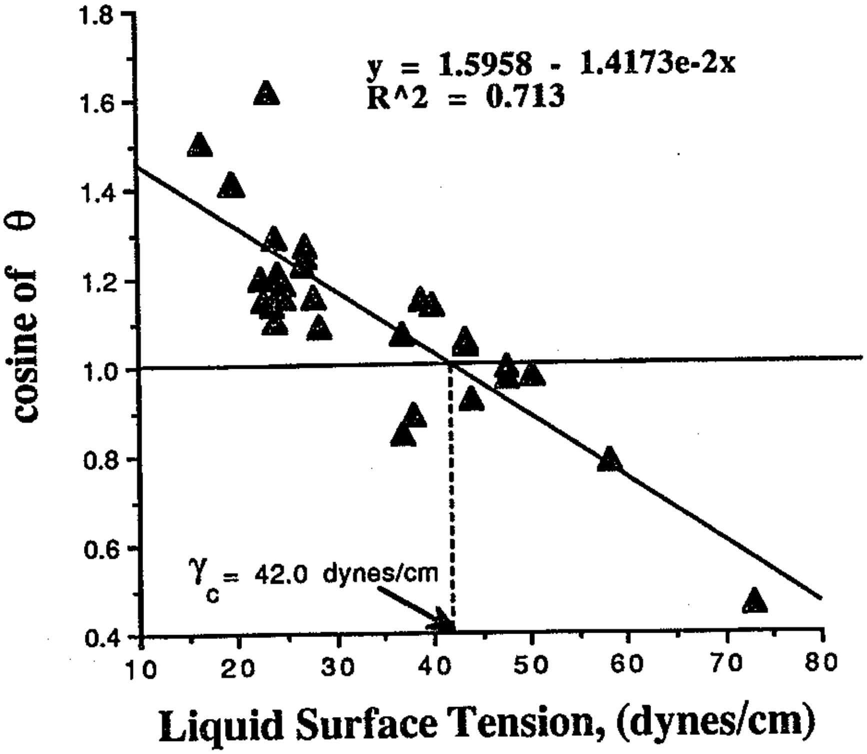

FIGURE 8-4. Determination of critical surface tension of sugar maple wood.

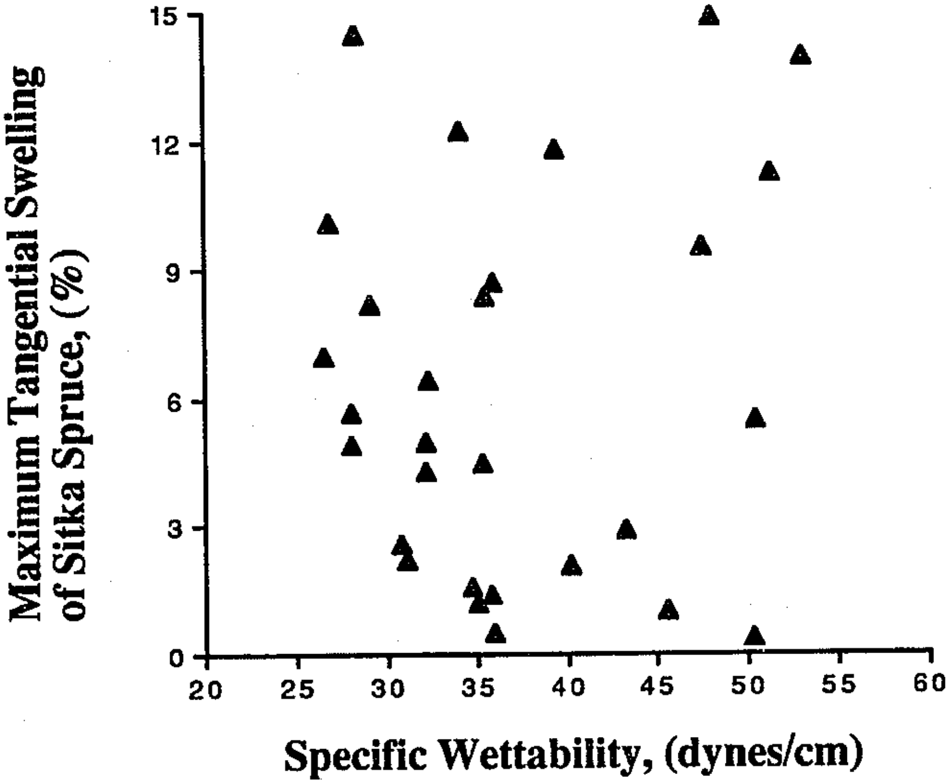

FIGURE 8-5. Maximum tangential swelling of wood plotted against wood specific wettability (sitka spruce).

lower interactions occurred with the acidic probe (ethylene glycol). The total surface free energy of wood ranged from 48.0 to 61.0 dynes/cm, on the average, and 75 to 80 % of this energy was attributed to the dispersion forces.

CHAPTER NINE

SWELLING OF COMPRESSED FIBERS IN WATER AND ORGANIC LIQUIDS

9.1. Introduction

Approximately 40 - 45 % of the wood dry substance is cellulose, located predominantly in the secondary cell wall. Bundles of cellulose molecules are aggregated together in the form of microfibrils in which highly ordered (crystalline) regions exist with less ordered (amorphous) regions. The proportions of crystalline and amorphous regions in cellulose vary depending upon the type of the sample and the method of measurement. Cotton cellulose is usually more crystalline than wood cellulose.

Cellulose is insoluble in most solvents because of its crystalline nature; however swelling is possible in the amorphous areas. Neale (1929), in his early work on cotton swelling in liquids, concluded that the action of a mild swelling agent is confined entirely to the amorphous portion of the fiber. As the fiber swells, intermolecular bonds are broken as a result of the internal stresses produced by swelling. The degree of order within the fiber is reduced and there is an increase in the surface area of the fiber. Also with very strong cellulose swelling agents, it is possible to reach a critical point where the entire crystalline structure of the fiber is disrupted and the fiber structure is lost. In this investigation an analysis is made of cellulose swelling in liquids which generally do not affect the crystalline structure of cellulose.

9.2. Results and Discussion

9.2.1. Effect of Bulk Density

Figures 9-1, 9-2, and 9-3 show the maximum liquid-holding capacity versus bulk density curves of α-cellulose, sulfite pulp, and thermomechanical pulp pellet swelling in water, methanol, and toluene, respectively. All maximum capacity curves showed a peak. Each curve, however, depending upon the type of the fiber and the swelling liquid, showed an optimum capacity in the region of a bulk density of 0.6 g/cc (α-cellulose in toluene) to 1.2 g/cc (thermomechanical pulp in water). Bulk densities below 0.4 g/cc were feasible to obtain but they did not result in a fiber pellet form with a workable shape. In addition, preliminary experiments showed that, below a specific bulk density of about 0.20 - 0.25 g/cc (non-compressed fiber systems), the contact of a fiber pellet with a liquid caused a reduction in the total volume. This observation is consistent with previous findings (Steiger and Kapur, 1972). The swelling action is due to the combined effect of both fiber cell wall swelling and loosening of the interfiber frictional bonds (curling or uncrimping) which involves fiber separation movements. The various crimps of the fibers in the pellet represent stored energy, with the higher the bulk density of a compressed fiber system, the higher the stored energy. Usually the fibers have the tendency to uncrimp rapidly on contact with water or another good swelling agent (formamide, methanol, etc.). The separating movement of the fibers thus results in expansion of the fiber volume and creates more room for the swelling solvent. In addition, the final maximum expansion of the fiber system depends, as mentioned, upon the absorbency of the fibers (fiber swellability) in the particular liquid, that is, the extent of swelling of the cell wall of the fibers. The shape and dimensions of the individual fibers will also affect the liquid interactions with the compressed fiber pellets. All these processes take place in the presence of the swelling liquid which, by means of its hydrogen bonding capability, molecular size and shape, cohesive energy density,

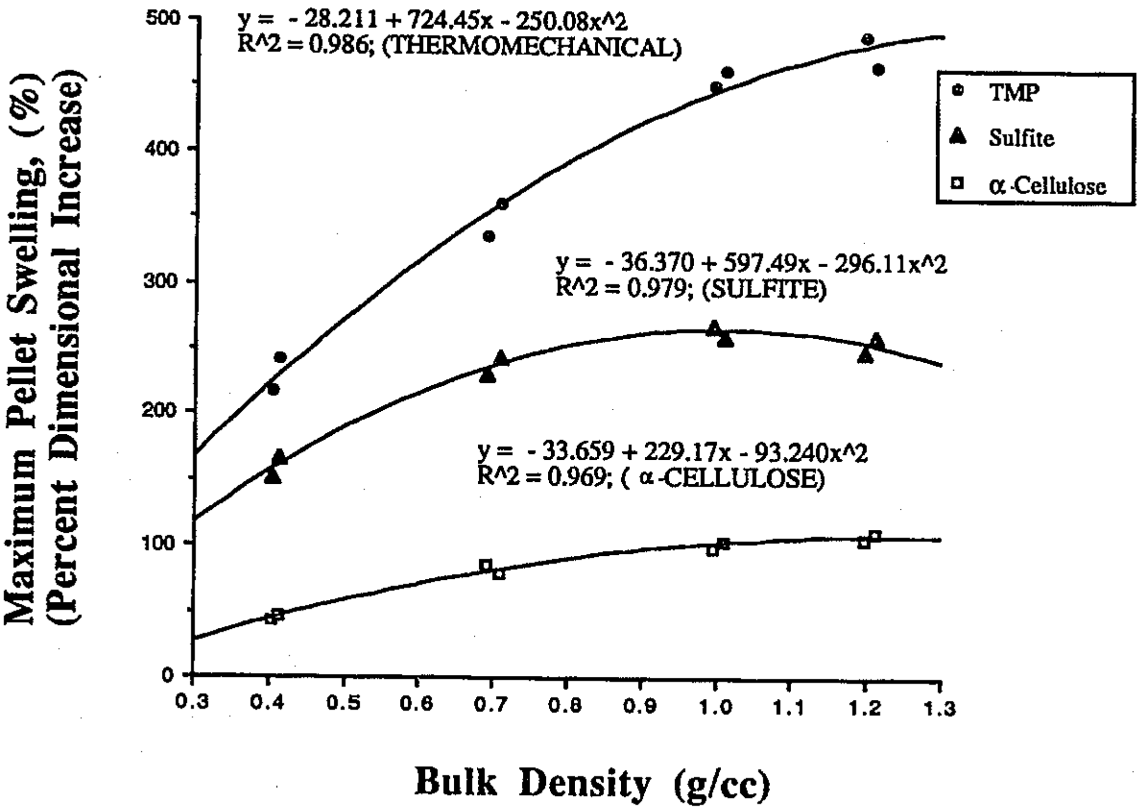

FIGURE 9-1. Maximum pellet swelling of fibers in water versus bulk density.

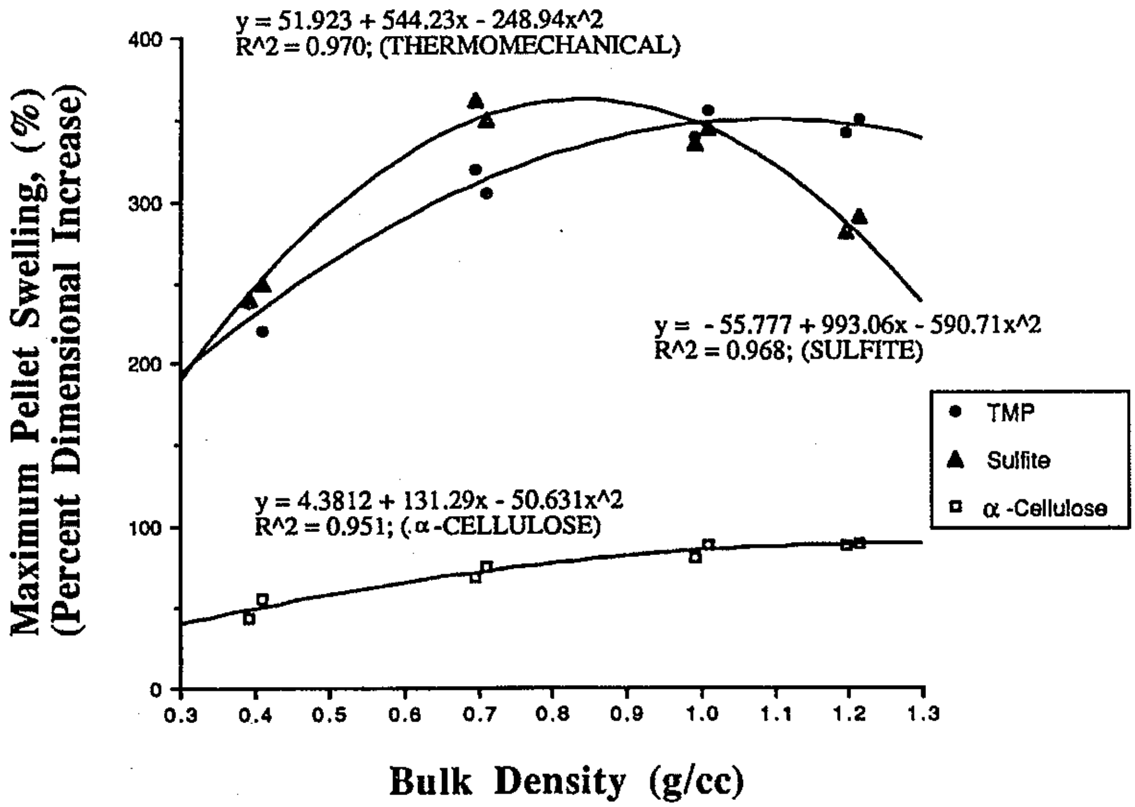

FIGURE 9-2. Maximum pellet swelling of fibers in methanol versus bulk density.

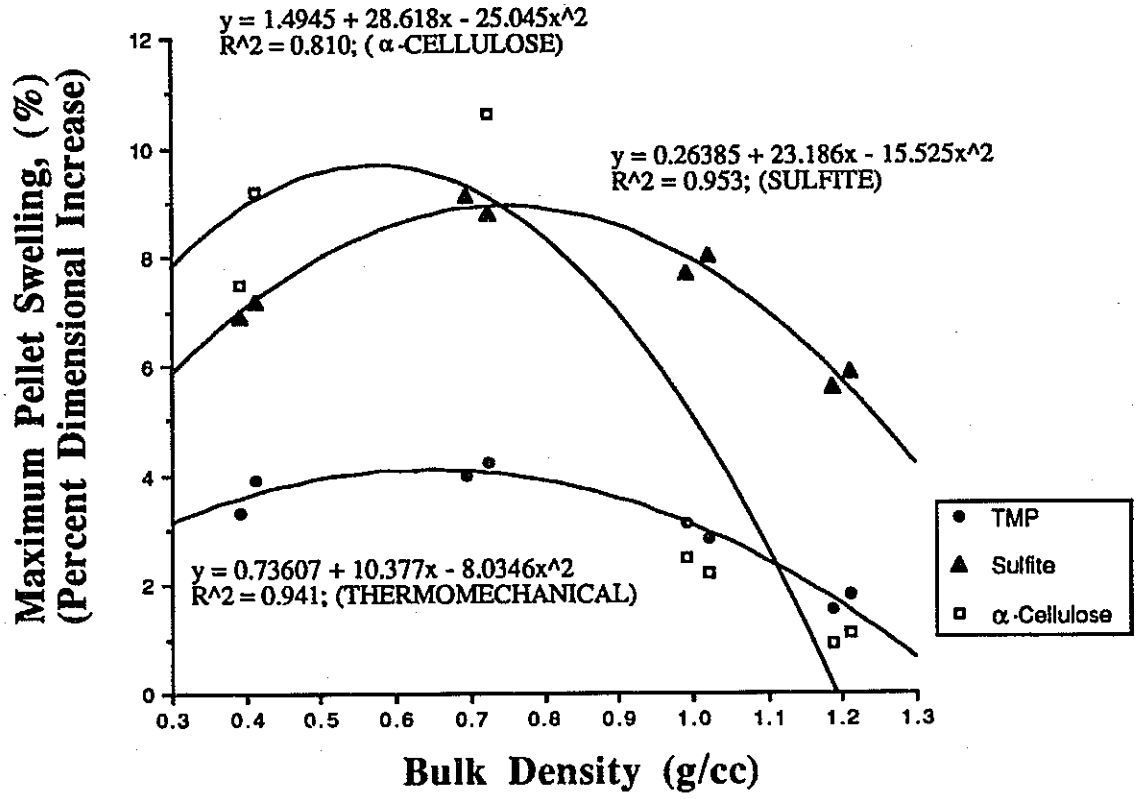

FIGURE 9-3. Maximum pellet swelling of fibers in toluene versus bulk density.

surface tension, etc., directs this expansion so that the fibers tend to align into better defined capillaries (Steiger and Kapur, 1972).

9.2.2. Compressed Fiber Swelling versus Wood Swelling

Figure 9-4 is a typical plot of the swelling of a thermomechanical pulp fiber pellet in ethanol at room temperature. The percent dimensional increase is plotted against time (min). The final equilibrium swelling of the pellet is reached after about 50 minutes. A small induction time is noted in this case; however, in most cases, no induction time was observed. The expansion of most fiber systems investigated in this work was relatively fast and, in some instances, almost instantaneous (i.e. water, formamide). Generally a swelling rate constant k is derived from the slope of the initial linear portion of the swelling profile. Similar measurements were made for all the compressed fiber systems in the various organic liquids (see Table 4-5).

The maximum liquid-holding capacities of α-cellulose and sulfite pulp in twenty various organic liquids at room temperature are shown in Table 9-1. The bulk density of the fiber systems was 0.5 g/cc. This density level was chosen to partially avoid the so-called "springback" effect at the higher densities which would give spuriously high final swelling values. For comparison, the maximum swelling values of spruce wood measured with a similar apparatus (tangential direction) in the same solvents (Chapter 6.2.1) are shown in Table 9-1. It is characteristic that liquids which swelled spruce wood to a low to medium degree (up to 6 % tangential swelling) did not swell α-cellulose and sulfite pulp fibers appreciably, while the good to excellent wood swelling agents (butylamine, DMSO, formamide, ethylene glycol, water, methanol, acetic acid, ethanol, and butyrolactone) swelled the pulp fibers to an appreciable extent (Figure 9-5). Results from Table 9-1 also indicate that butylamine, DMSO, formamide, and ethylene glycol swelled α-cellulose and sulfite pulp beyond the water-swollen

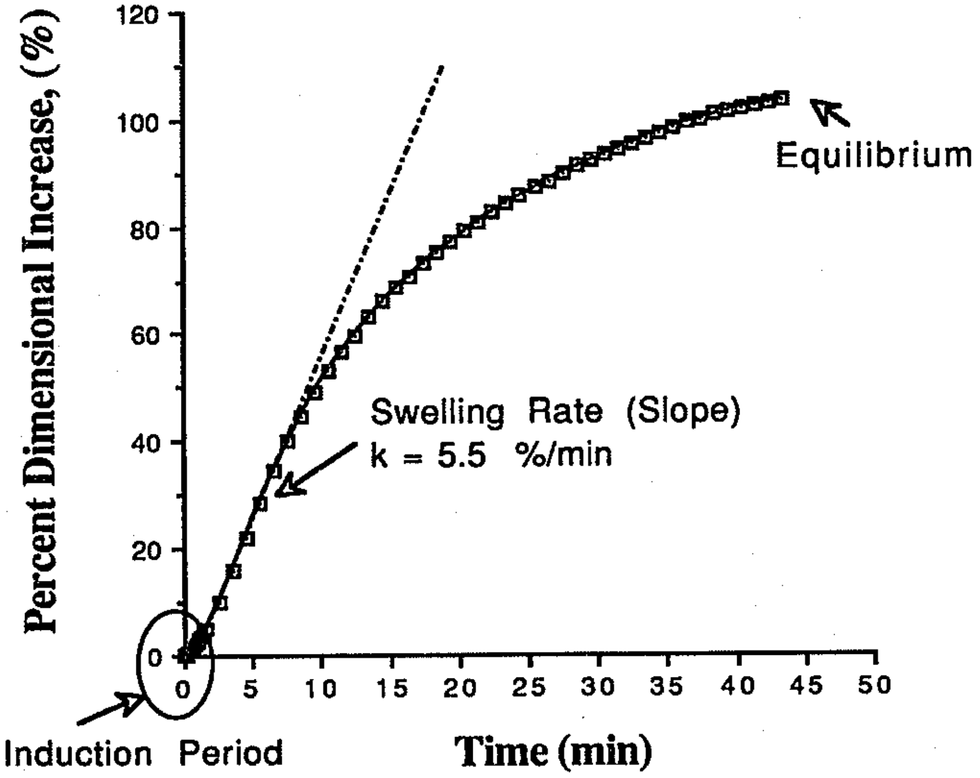

FIGURE 9-4. Swelling profile for compressed thermomechanical pulp fibers in ethanol at 23° C (pellet swelling).

TABLE 9-1

Maximum Liquid-Holding Capacities (Percent Dimensional Increase) of α-Cellulose and Spruce Sulfite Pulp, and Maximum Tangential Swelling of Spruce Wood in Various Organic Liquids

Liquids	α-Cellulose (%)[1]	Sulfite (%)[1]	Spruce wood (%)[2]
Water	85.3	403.0	8.4
Methanol	83.4	293.6	8.2
Ethanol	41.7	109.4	7.0
Formamide	179.6	470.7	11.2
Ethylene glycol	180.0	463.0	9.5
Pyridine	51.0	461.9	12.2
Dimethylsulfoxide	202.4	563.0	13.9
Acetic acid	76.4	280.4	8.7
Butylamine	209.6	601.8	14.5
Propanol	25.4	18.4	4.9
Dioxane	20.8	16.2	5.7
Acetone	13.4	47.6	5.7
Ethylacetate	18.9	5.9	2.6
Methylacetate	20.3	21.7	5.0
Nitromethane	29.4	45.3	4.5
Butyrolactone	33.4	96.0	7.2
Benzyl alcohol	39.6	10.0	2.9
Carbon tetrachloride	13.0	8.9	1.2
Toluene	8.0	11.6	1.6
Ethylene dichloride	15.3	17.3	2.1

[1] Average of two replicates (fiber pellet density ~ 0.5 g/cc).
[2] Data from Chapter 6.2.1 (spruce density ~ 0.4 g/cc).

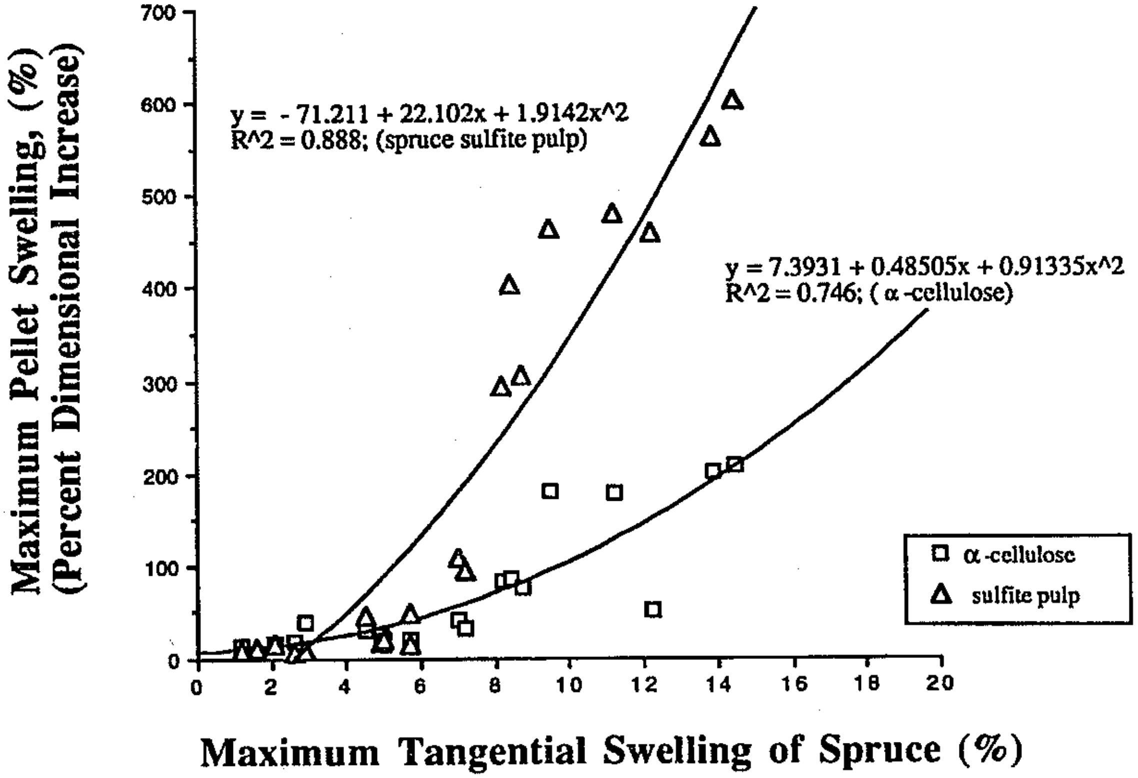

FIGURE 9-5. Maximum pellet swelling of fibers versus maximum tangential swelling of spruce in various organic liquids at room temperature.

dimensions. The largest increases were caused by butylamine and DMSO. On the other hand, toluene, carbon tetrachloride, ethylene dichloride, and ethyl acetate resulted in the lowest maximum liquid-holding capacities of the compressed fiber pellets. Notable was the swelling behavior in pyridine which exhibited a very high swelling power on sulfite pulp fibers but it swelled α-cellulose only to a medium extent (lower than that of water). This result is possibly due to the strong swelling power of pyridine on the lignin in the cell wall of the sulfite pulps. The maximum liquid-holding capacities obtained within the homologous series of alcohols were in a descending order (Water > MeOH > EtOH > PrOH), an expected result based on previous investigations (Stamm, 1935; Stamm, 1964).

We divided the swelling liquids into five different chemical classes (see Table 4-5) based upon three solvent properties (molar volume, CED, and hydrogen bonding capability). Results for α-cellulose pellet swelling within the five classes versus CED are plotted in Figure 9-6. The relationships shown in Figure 9-6 are very similar with those reported in our previous experiment on the swelling of wood (Chapter 6.2.1) and cellulose (Robertson, 1964) in organic liquids. It was also found that a rough linear correlation existed between the maximum liquid-holding capacity of α-cellulose in seventeen various organic liquids and the cohesive energy density of the swelling liquid (Figure 9-7). This trend indicates that, in general, the higher the solvent CED, the higher the α-cellulose swellability (pellet swelling). A similar relationship was also reported by Thode and Guide (1959) for the cellulose maximum swelling behavior in several organic solvents (against solubility parameter). However in Figure 9-7 there were three exceptions (butylamine, DMSO, and water). Generally, the liquids with a high molar volume (toluene, ethyl acetate) or a low hydrogen bonding parameter (ethylene dichloride, carbon tetrachloride, nitromethane) caused very low cellulose

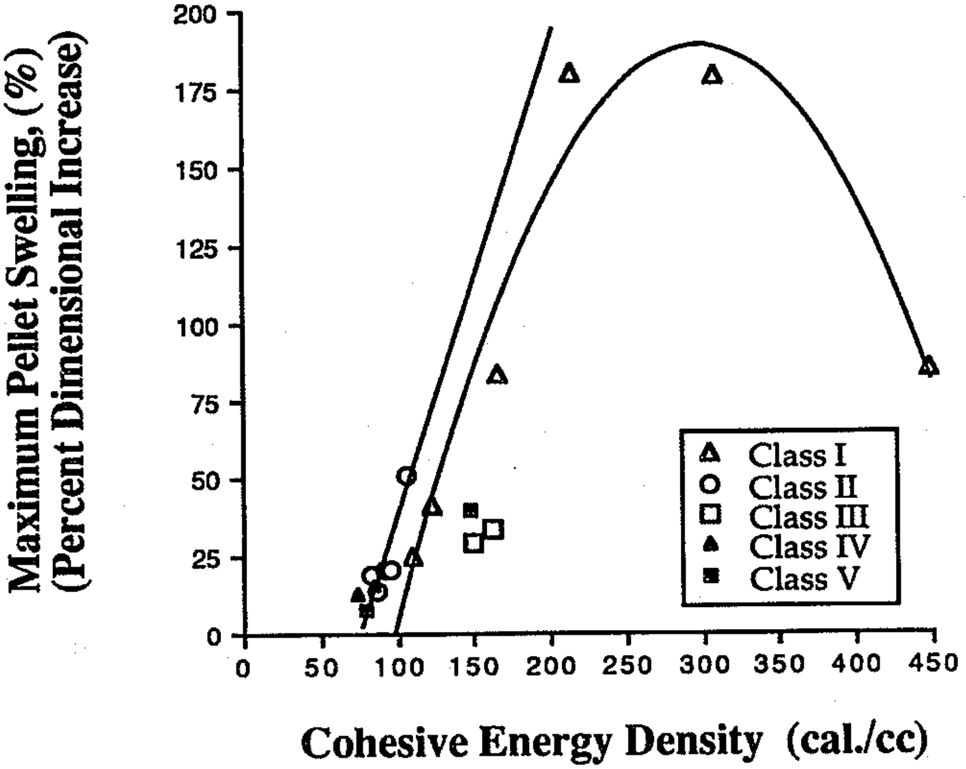

FIGURE 9-6. Maximum pellet swelling of α-cellulose versus solvent cohesive energy density within various solvent chemical classes.

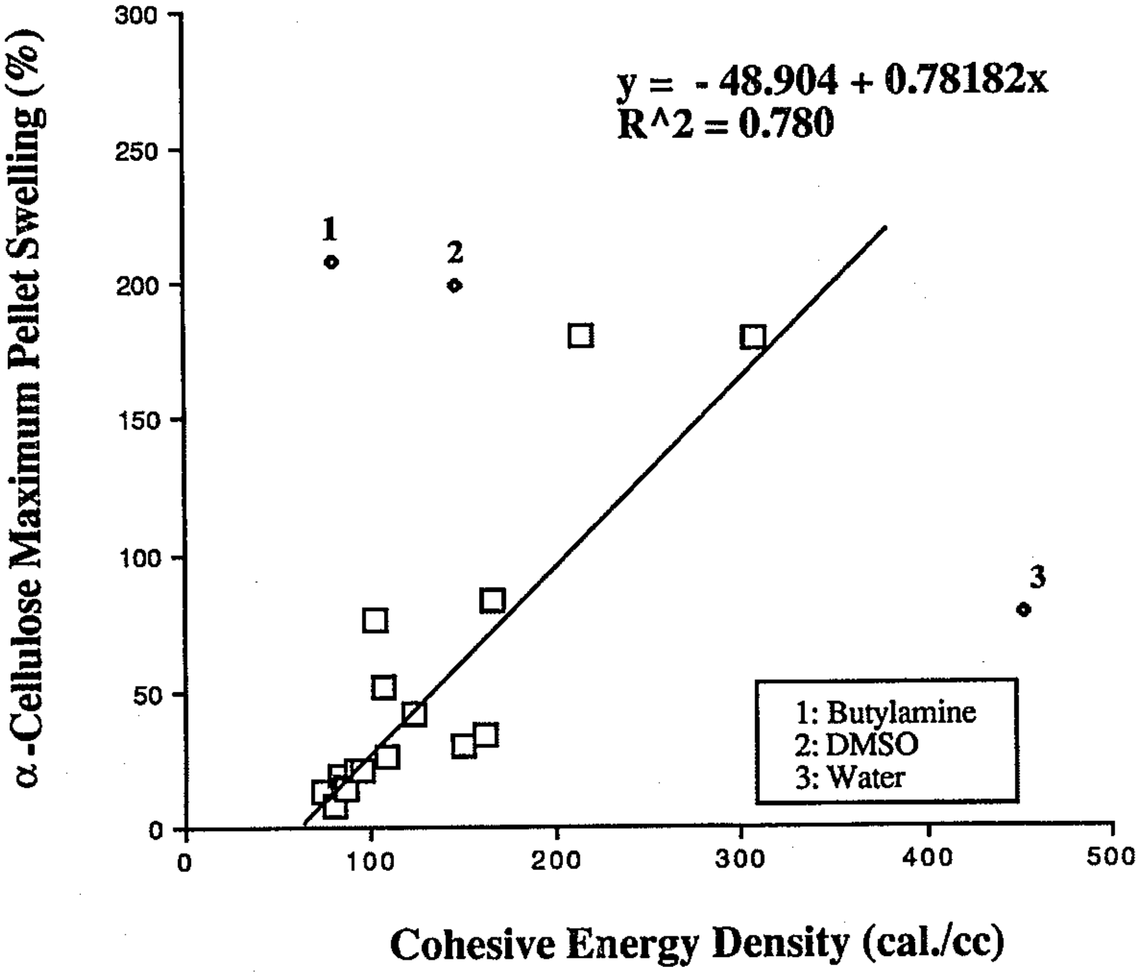

FIGURE 9-7. Maximum liquid-holding capacity of α-cellulose pellets in various solvents versus solvent CED.

pellet swelling. The very high swelling power of butylamine, whose molar volume is quite high, is explainable based on its very high hydrogen bonding capability. It has been reported that amines can penetrate even the highly ordered (crystalline) regions of the cellulose fibers (Thode and Guide, 1959). It was also found that organic liquids with a high hydrogen bonding parameter (HBP) (Lieberman, 1962) swelled α-cellulose and sulfite pulp to the greatest extent (Figure 9-8). Each column in Figure 9-8 represents the average maximum liquid-holding capacity (fiber swellability) in each solvent class (high, medium, and low HBP). Similar results were also reported for the wood swelling in organic liquids (Figure 6-13). However, exceptions to this include the swelling in propanol (α-cellulose and sulfite) and in pyridine (α-cellulose).

Overall, it can be said that the hydrogen bonding capability of the swelling liquid seems to be the most important factor in the whole process which is in accord with the literature (Stamm and Tarkow, 1950; Mckenzie, 1956; Robertson, 1964; Philipp, 1973). However, the properties of liquids that determine their effectiveness in interaction with isolated cellulose or cellulosic fibers obviously cannot be assessed by just one or two individual parameters (Robertson, 1964). Besides hydrogen bonding, molar volume, and cohesive energy density, other properties such as steric hindrance and molecular shape or branching are also important and must be considered (Robertson, 1964).

9.2.3. Swelling of Various Compressed Fibers in Water and Organic Liquids

The data presented in Table 9-2 show the maximum liquid-holding capacities (maximum pellet swelling) of nine different compressed fibers in ten various organic liquids at room temperature. The average pellet bulk density of all the fiber systems was 0.5 g/cc. In general, most fiber pellets exhibited the highest liquid-holding capacities with butylamine, DMSO, formamide, water, and acetic acid (in an approximate

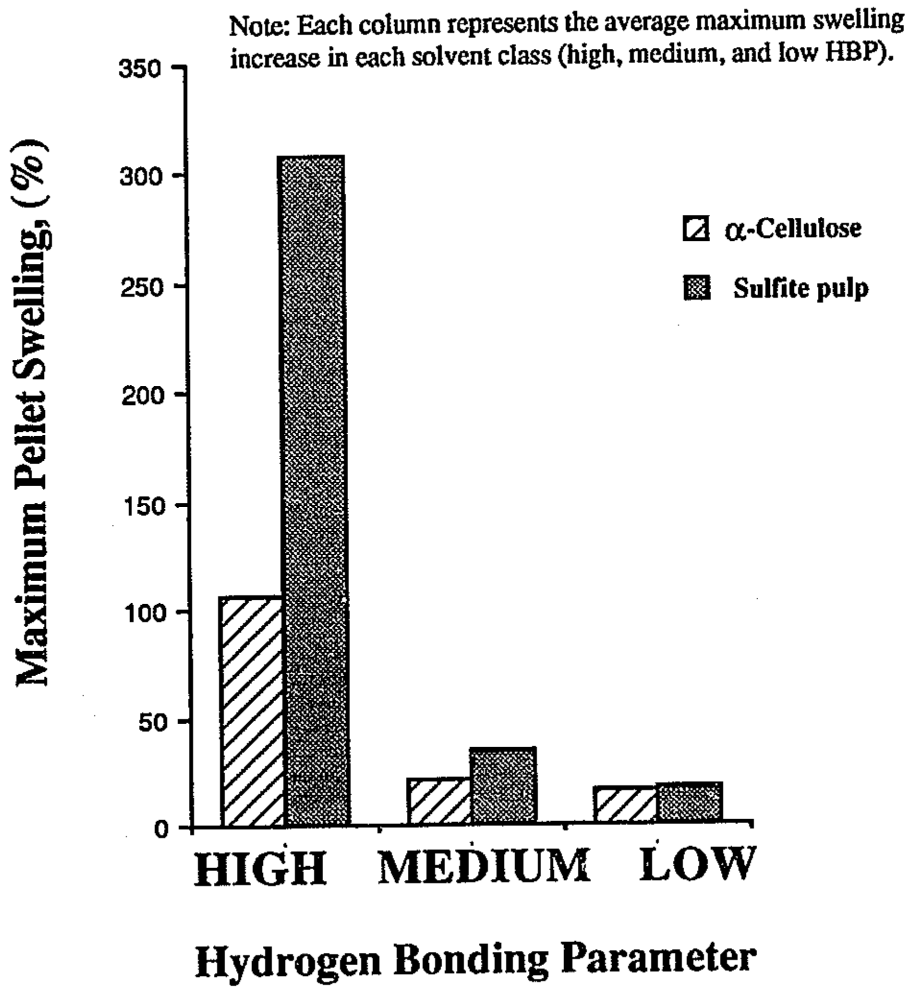

FIGURE 9-8. The effect of the hydrogen bonding parameter on the maximum pellet swelling of compressed fibers.

TABLE 9-2

Maximum Liquid-Holding Capacities (Percent Dimensional Increase) of Various Compressed Fiber Systems in Organic Liquids at 23° C

	Fibers[1]								
	alpha-Cellulose	Avicell	TMP	Sulfite	Kraft	Aspen fiber	Filter Paper	Cotton	Rayon
Liquids									
Water	85.0	60.9	382.1	391.2	373.8	340.1	233.1	355.2	379.2
Formamide	168.9	74.0	392.3	480.1	479.9	475.3	365.4	465.7	431.8
Pyridine	46.4	89.7	432.1	459.4	332.9	474.2	296.1	35.3	22.1
Acetone	14.7	5.9	78.4	35.6	43.1	110.0	21.1	19.7	18.7
Nitromethane	26.4	5.7	66.9	34.7	50.4	123.2	24.9	22.1	27.2
Ethylene dichloride	16.5	2.2	10.3	15.1	13.0	25.1	7.7	6.5	17.7
Toluene	10.6	1.4	3.9	8.8	5.6	5.9	6.7	5.4	14.4
DMSO	190.5	67.4	523.7	502.0	574.9	455.5	427.8	691.0	452.5
Acetic acid	87.9	59.1	274.6	305.4	316.8	305.9	183.4	356.1	57.5
Butylamine	225.0	103.7	503.1	630.1	691.6	497.4	517.2	640.1	595.4

1: Average of two replicates (pellet bulk density = 0.5 g/cc).

descending order). Pyridine was an excellent swelling agent for fiber pellets from thermomechanical pulp, sulfite pulp, kraft pulp, aspen fiber, and filter paper. It did not however swell appreciably pellets from cotton, rayon (regenerated cellulose), and α-cellulose (lower than water). The low hydrogen bonding capability as well as high molecular volume liquids such as toluene and ethylene dichloride had, as expected, the lowest swelling powers on all of the fiber pellets, especially for avicell and cotton (almost negligible). α-Cellulose pellets swelled more than avicell pellets in all the solvents (except in pyridine) (Figure 9-9). This result can be expained by the very high degree of crystallinity of avicell. Pyridine and butylamine proved to be the most powerful swelling agents for avicell. Also, formamide, DMSO and butylamine swelled α-cellulose pellets more than twice as high as avicell pellets.

McKenzie (1956), using a mercury dilatometer, measured swellabilities of eucalypt α-pulps in various solvents and a comparison with our results on α-cellulose is shown in Table 9-3 (A). Sitka spruce sulfite and kraft pulp fiber pellets swelled to almost the same extent in liquids such as formamide, acetone, ethylene dichloride, and acetic acid. Sulfite pulp pellets swelled slightly higher than kraft pellets in water; in accord with previous findings (Fernandez, 1993; McKenzie et al., 1960; von Koeppen, 1964). For comparison purposes, the chemical composition of sulfite and kraft pulp fibers is shown in Table 9-4. In addition, pyridine swelled sulfite pulp pellets much higher than kraft, while DMSO and butylamine swelled kraft pulp pellets higher than sulfite (Figure 9-10).

Philipp et al. (1973) measured the maximum liquid retention values (LRV) of spruce sulfite pulp samples; his results are compared with the maximum liquid-holding capacity of compressed fiber pellets from the present work (Table 9-3, (B)). Except in pyridine, there is a good relative correlation of the swelling results in the various

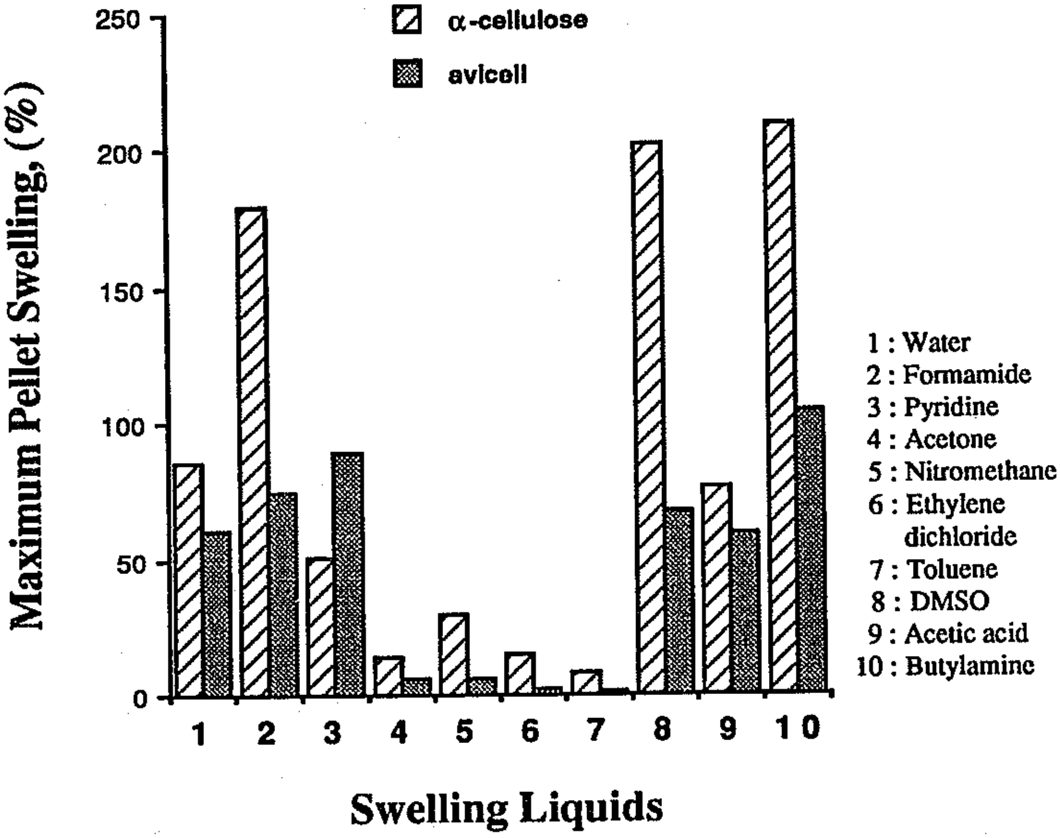

FIGURE 9-9. Comparison of α-cellulose versus avicell maximum pellet swelling in various organic liquids.

TABLE 9-3

Swelling Power of Various Reagents on Cellulosic Fibers

REAGENT		**SWELLING INDEX**
(A)	**McKenzie (1956)**	(Mercury Dilatometer Measurements)
	Oven-dry cellulose eucalypt α-pulp, Volume Swelling, (%)	Present Work commercial α-cellulose, Thickness Direction Swelling; (%)
Acetone	27.6	14.7
Ethanol	42.0	41.7
Water	117.6	85.0
Pyridine	120.0	51.0
Formamide	133.2	168.9
(B)	**Philipp et al. (1973)**	(Swellability Relative to that of Water)
	Liquid Retention Values Max. (1 hr./20° C)	Present Work Max. Liquid-Holding Capacity; (%); (24 hrs./23° C)
	Spruce Sulfite Pulp	Spruce Sulfite Pulp
DMSO	192.0	139.7
Formamide	134.9	116.7
Ethylene glycol	133.3	114.9
Water	100.0	100.0
Acetic acid	71.4	69.5
Pyridine	68.3	114.6 (!)
Methanol	52.4	72.8
Ethanol	50.8	27.2
(C)	**Robertson (1970)**	(Swellability Relative to that of Water)
	Caliper Measurements of Immersed Paper, (%)	Present Work Filter Paper, (%)
Acetone	2.6	9.0
Acetic acid	44.7	78.6
Water	100.0	100.0
Pyridine	100.0	127.3
Formamide	136.8	156.7
DMSO	189.5	183.5

TABLE 9-4

Properties of Sitka Spruce Kraft and Sulfite Pulps (Fernandez, 1993)

Properties:	Kraft	Sulfite
Klason Lignin (%)	7.4	8.0
Residual Lignin (gr/gr)	3.7	4.6
Residual Glucan (gr/100gr)	38.1	46.2
Residual Xylan (gr/100gr)	6.1	2.2
Residual Mannan (gr/100gr)	1.5	2.1
Specific Wettability (advancing) with Water (dynes/cm)	38.0	40.2

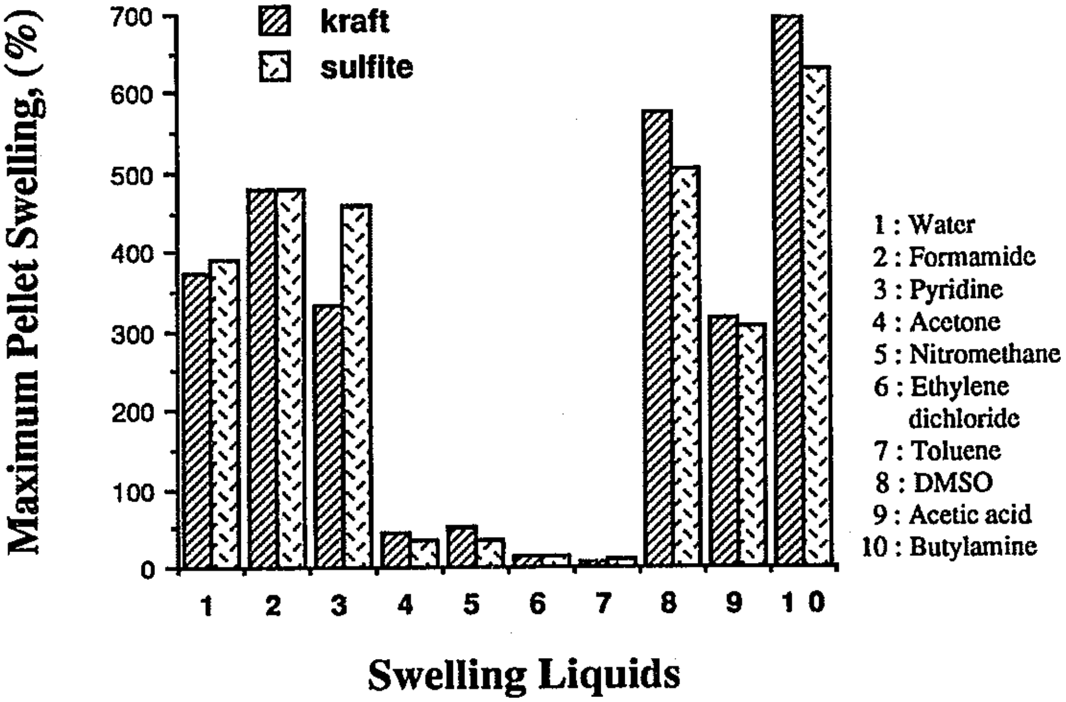

FIGURE 9-10. Comparison of spruce sulfite versus spruce kraft pulp maximum pellet swelling in various organic liquids.

solvents using the two different approaches. Pyridine was an excellent swelling agent for thermomechanical pulp pellets (loblolly pine; 95 % yield). Acetic acid did not swell rayon pellets as significantly as it did with the rest of the fiber pellets (Table 9-2).

Swelling measurements on compressed disintegrated filter paper (density = 0.5 g/cc) in ten organic liquids were also done in this work. Filter paper pellet swelling results are compared with Robertson's (1970) results also shown in Table 9-3 (C). Robertson made caliper measurements on immersed paper samples in several organic liquids. Robertson's swellability values for paper in Table 9-3 (C) are relative to those in water since he made no reference to the apparent density of the paper in his work. Generally the results are in good relative agreement.

Figure 9-11 is a plot of the maximum swelling (percent increase in thickness direction) of aspen wood fiber pellets versus the maximum tangential swelling of aspen wood (Chapter 6.2.1; see Table 6-1) in ten various organic liquids. The almost linear correlation indicates that these particular liquids produced almost analogous swelling effects on both wood and wood fibers (same wood species).

The liquid retention values (LRV) of various types of cellulosic fibers in ten organic liquids at room temperature are shown in Table 9-5. It must be emphasized that LRV is an empirical estimate of the swollen volume of fibers and cannot be considered as an unbiased measure of the degree of fiber swelling. However, the overall LRV methodology has gained considerable acceptance in recent years. It is obvious from the results in Table 9-5 that the structure and type of cellulose (pulps, cotton, wood species, etc.) influence the fiber swelling behavior (measured as LRV) in different organic liquids whose swelling power varies greatly. Solvents such as DMSO, formamide, and ethylene glycol, as expected, resulted in higher fiber liquid retention values than those of water. The low hydrogen bonding and high molecular volume toluene and ethylene

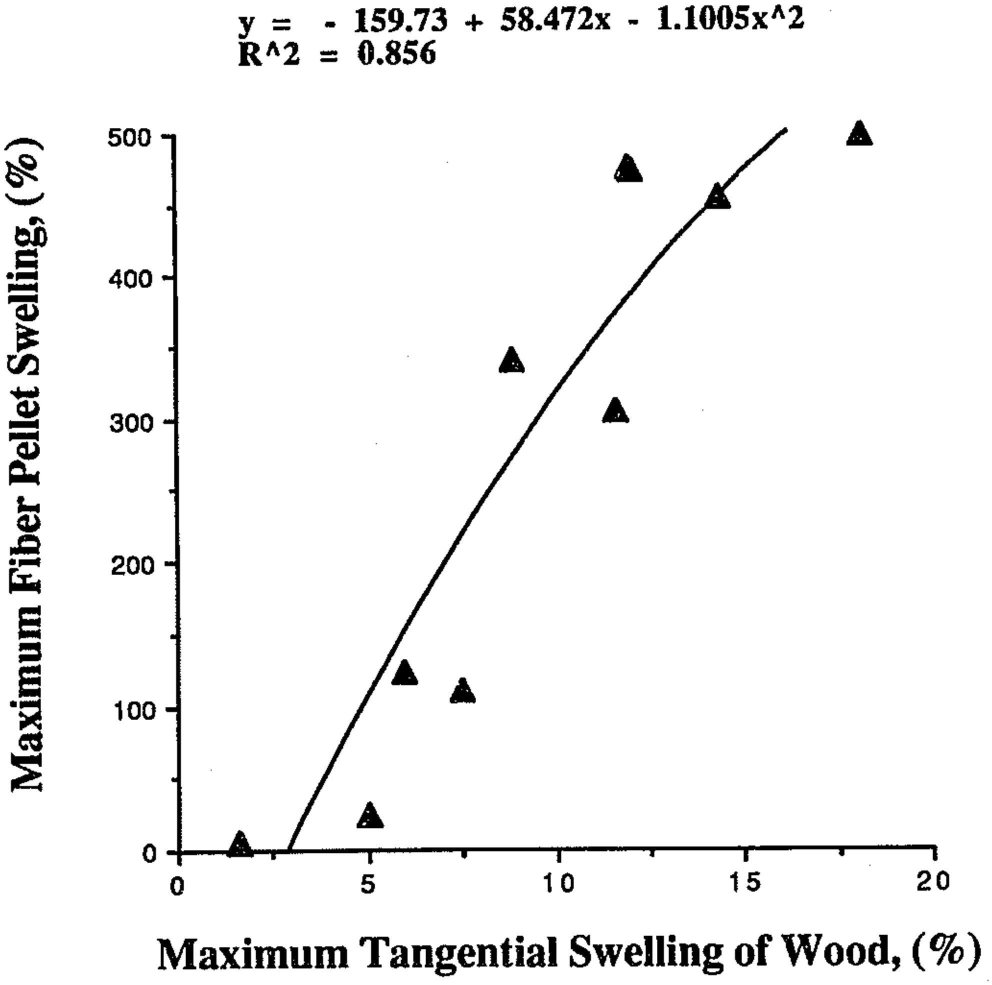

FIGURE 9-11. Maximum tangential swelling of wood versus maximum fiber pellet swelling in various organic liquids (quaking aspen).

TABLE 9-5

LRV of Cellulose Fiber Samples in Various Liquids, (%)

(Swelling time 2 hrs./23° C)

Swelling liquid	Spruce Sulfite	Spruce Kraft	TMP	Aspen Fiber	Filter Paper	Cotton
Water	97.4	92.4	58.6	64.9	75.2	42.3
Methanol	76.8	61.3	35.1	44.0	24.1	16.1
Ethanol	72.2	54.4	31.1	34.9	19.2	13.2
Nitromethane	45.2	32.2	6.3	21.4	7.5	9.1
Ethylene dichloride	15.2	22.1	1.1	1.3	1.5	3.1
Toluene	27.0	24.9	1.6	3.5	2.1	5.8
DMSO	168.4	162.6	112.5	127.7	127.0	64.4
Acetic acid	76.4	55.2	19.9	37.1	19.2	12.9
Ethylene glycol	132.6	126.5	93.2	95.1	80.1	52.5
Formamide	155.7	149.3	97.7	114.4	102.0	57.4

dichloride caused the lowest LRV, almost independent of the type of fiber, and had the lowest swelling powers. LRV data for spruce sulfite pulps in seven liquids are in relatively good agreement with LRV data reported by Philipp et al. (1973); our results are slightly higher (approximately 1.3 times, on the average). Sulfite pulp had a liquid retention value with water, (WRV), slightly higher than that of kraft pulp; in accord with the maximum liquid-holding capacity results (Table 9-2). A comparison between the LRV and pellet maximum liquid-holding capacity also reveals that both sulfite and kraft pulps had an almost analogous swelling behavior in most of the swelling liquids.

It was found that the time necessary to reach an apparent maximum LRV in most of the liquids was usually less than one hour, except for cotton fibers whose LRV were very low even after two hours of swelling. Generally, cotton swelled in most liquids very slowly possibly due to its higher degree of crystallinity (LRV for cotton was thus measured after 24 hours of swelling). Overall, no general relation between LRV and the solvent parameters such as density, viscosity or surface tension was found; consistent with the literature (Stamm and Tarkow, 1950; Philipp et al., 1973). In addition, no clear correlations existed between LRV and any of the individual parameters commomly used to characterize cellulose interactions with organic liquid molecules such as dipole moment, dielectric constant, and solubility parameter. However, it appears that a moderate trend exists between LRV and liquid molar volume (MV), that is, in general, as the MV increases, the LRV decreases gradually, especially when a high MV is associated with a low hydrogen bonding capability (ie. toluene). Also, a linear positive trend exists between LRV and solvent cohesive energy density (with the exception of water which has an extremely high CED). Indeed, all fibers used in this work had their highest LRV interactions with the high CED liquids such as DMSO, formamide, ethylene glycol, water, and methanol. Overall, no general relationship was found between LRV of various types of cellulose fibers and one single parameter of the swelling liquid; but rather the final LRV is determined mainly by the interrelation between molar volume, hydrogen bonding capability, and cohesive energy density, and also is influenced by the molecular and morphological structure of the cellulose fiber.

9.2.4. Effect of Temperature

Swelling rates, k, and activation energies, Ea, for fiber pellet swelling (TMP, sulfite pulp, aspen fiber, and filter paper) in several organic liquids are presented in Table 9-6. The calculation of activation energies was done for comparison purposes, but theoretically, fiber spring-back and uncurling in fiber pellet swelling do not involve chemical transition states; however the high R^2 values obtained indicate significant dependence of fiber pellet swelling on temperature, and fiber pellet swelling appears to obey the classical Arrhenius equation (Eq. 4.2).

Figure 9-12 shows the rate of pellet swelling of a thermomechanical pulp fiber (loblolly pine) in methanol at three different temperatures. It is apparent that the rate increased almost three times from room temperature (23°) to 60° C. The activation energy of swelling, Ea, was then calculated using the Arrhenius equation (Figure 9-13). In general, the Arrhenius plots showed strong linear correlations with high R^2 (Table 9-6).

Generally the swelling of the compressed fibers in ethanol and ethylene glycol had the highest dependences upon the temperature (Ea) while the fiber swelling in the low molar volume liquids such as water and methanol showed the lowest Ea. It should be stressed that the swelling rates in water, formamide, and methanol were extremely high, that is, pellet fiber swelling increases were almost instantaneous. It was also noted that the swelling rates of compressed disintegrated filter paper were the lowest in all the

TABLE 9-6

Swelling Rates (k) and Activation Energies (Ea) for
the Swelling of Compressed Fibers in Several Organic Liquids

		Thermomechanical			Sulfite			Filter Paper			Aspen Fiber		
Solvents:	T (Celsius)	k (%/min)	Ea (KJ/mol)	R^2	k (%/min)	Ea (KJ/mol)	R^2	k (%/min)	Ea (KJ/mol)	R^2	k (%/min)	Ea (KJ/mol)	R^2
	23	4631.7			638.0			2769.1			3877.8		
WATER	40	6433.9	10.7	0.954	1264.5	31.8	1.000	4147.0	17.3	0.999	4707.5	11.1	0.987
	60	7518.9			2686.9			6055.4			6389.2		
	23	577.6			324.6			86.3			762.6		
METHANOL	40	971.3	21.3	0.996	585.4	25.2	0.999	182.9	25.8	0.970	1534.4	29.4	0.998
	60	1509.3			1011.8			277.0			2880.0		
	23	5.5			3.5			0.63			4.8		
ETHANOL	40	27.8	68.3	0.998	10.0	50.6	0.999	2.8	78.8	0.994	48.1	84.1	0.982
	60	120.4			34.4			22.0			215.6		
	23	11.1			31.8			24.9			11.2		
ETHYLENE GLYCOL	40	89.9	66.1	0.944	136.2	49.9	0.968	68.9	37.0	0.981	61.6	71.9	0.998
	60	221.4			303.5			132.7			288.6		
	23	553.6			658.6			369.4			609.4		
FORMAMIDE	40	1745.8	33.7	0.915	1324.5	24.7	0.976	736.6	25.5	0.984	1273.9	29.5	0.994
	60	2553.4			2012.0			1169.5			2307.7		
	23	167.3			145.5			90.2			345.3		
DMSO	40	524.1	46.8	0.996	737.2	51.8	0.948	348.9	44.3	0.956	1268.2	46.0	0.976
	60	1384.7			1519.6			669.9			2765.3		

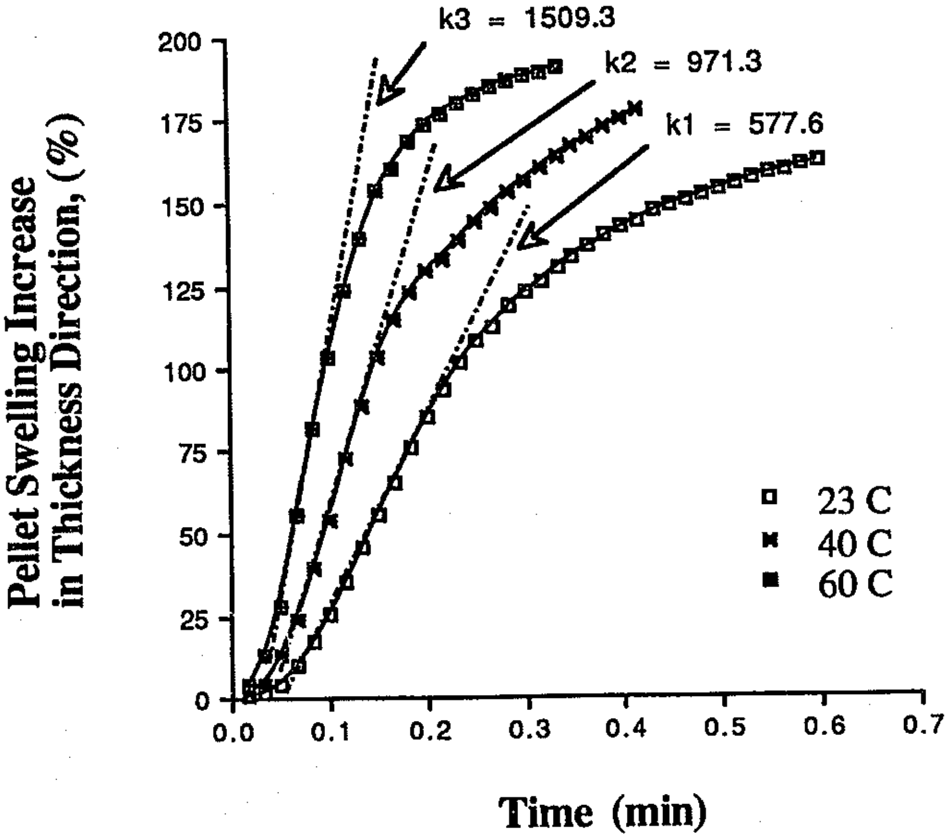

FIGURE 9-12. Thermomechanical pulp pellet swelling in methanol at various temperatures.

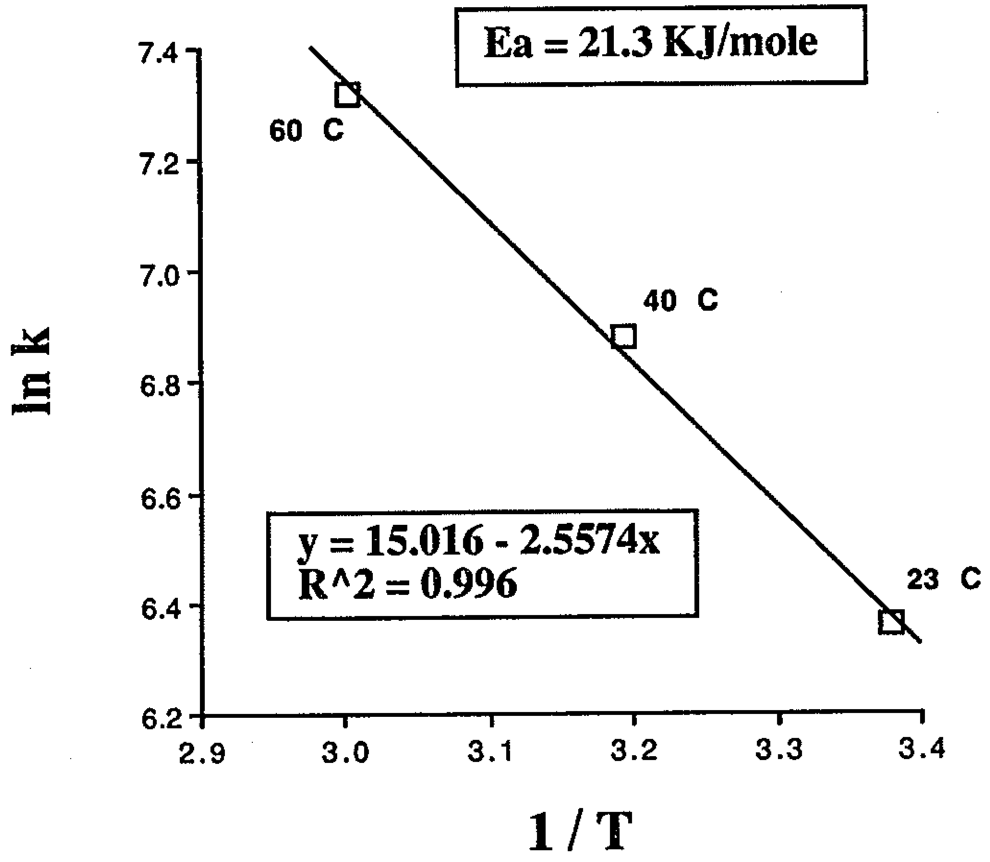

FIGURE 9-13. Arrhenius plot for calculation of activation energy (Ea) for TMP pellet swelling in methanol.

liquids investigated except in water.

The rate of compressed fiber swelling was mainly affected by the molecular size of the swelling liquid (Figure 9-14), that is, in general, the larger the solvent molar volume, the larger the Ea. Similar trends have also been obtained for the wood swelling Ea in several liquids (Chapter 6.2.4; see Figure 6-18). Future work on the swelling of compressed fibers in a more extensive series of organic solvents (various chemical classes) should provide additional information and a better understanding of the whole process. However, it has been noted that liquids with a molar volume greater than 100 - 110 cc are relatively inactive in wood pulp and cotton studies (Robertson, 1964). It is anticipated therefore that the temperature effect on such interactions would be of significant importance.

A polynomial trend was additionally found to exist between Ea of pellet swelling and cohesive energy density of the swelling liquid in filter paper (pure cellulose) (Figure 9-15). The R^2 of this correlation was 0.631. This indicates that, in general, the lower the CED of the swelling liquid, the higher the Ea of paper pellet swelling. This result is in good agreement with Robertson's (1964) conclusion that, assuming that the CED of cellulose is high, the greater interactions of cellulose should result with liquids having the higher cohesive energies.

9.3. Summary

Hydrogen bonding capability, molecular size, and cohesive energy density of the swelling liquid appeared to be the most important parameters in the swelling of various cellulosic fibers in organic liquids (compressed fiber systems). Correlations between cellulose compressed fiber pellets and wood swelling in the various liquids were generally quite good. It was also found that the temperature had a large influence on the

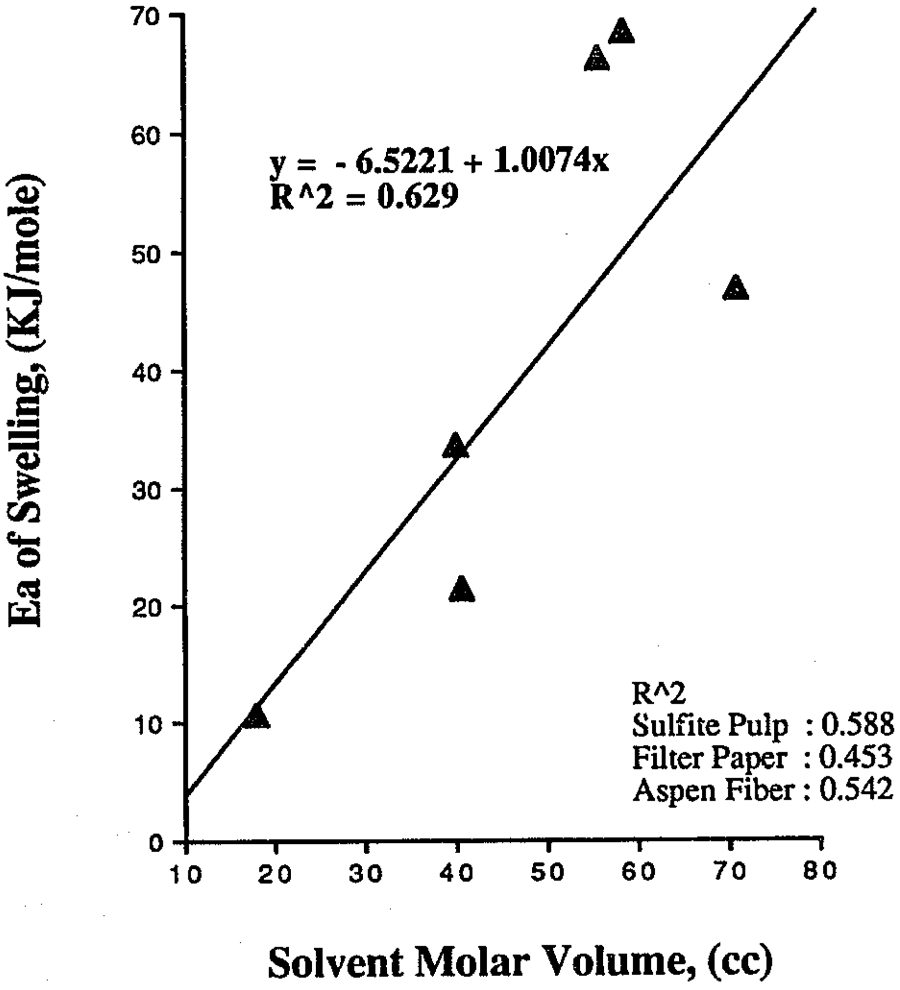

FIGURE 9-14. Ea of swelling of TMP compressed fibers in several liquids versus solvent molar volume.

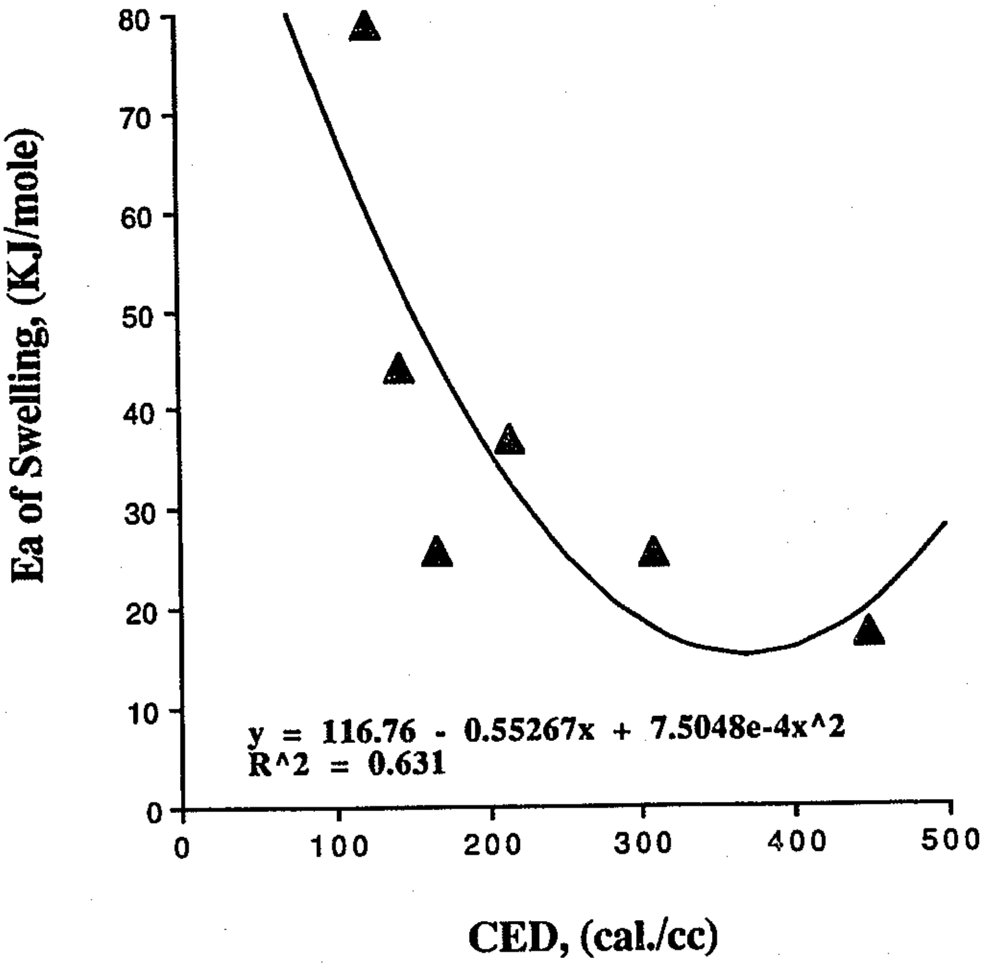

FIGURE 9-15. Ea of filter paper pellet swelling versus solvent cohesive energy density.

rate of swelling of four types of compressed fibers in several solvents. Activation energies (Ea) for the compressed fiber swelling in six liquids were evaluated with a computerized LVDT. Ea was linearly correlated with the solvent molar volume.

CHAPTER TEN

SUMMARY AND CONCLUSIONS

The rate and maximum swelling of several North American wood species in water have been obtained with a computer interfaced linear variable displacement transformer (LVDT). Since wood swells extremely rapidly in water even at room temperature, this apparatus made it possible to obtain accurate rate data on the swelling of wood in water. The strict linear dependence of swelling on the temperature suggests a chemical mechanism. The activation energies obtained from Arrhenius plots ranged from 32.2 KJ/mole for sitka spruce to 47.6 KJ/mole for sugar maple. Although the two hardwoods exhibited greater maximum tangential swelling compared with the two softwoods, the maximum swelling appears to be correlated with the wood density. Generally both the rate and maximum swelling of the woods were increased by removal of extractives and the activation energies were reduced.

The rate and maximum swelling of several North American wood species in forty organic liquids have also been obtained with the same LVDT. Since wood swells also very fast in some organic liquids, even at room temperature, this apparatus made it possible to obtain accurate wood swelling rate data 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 swelling of wood. All 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 (ln 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 ln k 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 solubility parameter, dipole moment, dielectric constant, and surface tension showed very weak correlations with the maximum tangential swelling of wood in organic liquids. Maximum swelling of wood in organic solvents was primarily influenced by three solvent properties, solvent basicity, molar volume and hydrogen bonding capability.

The swelling of wood in organic liquids at elevated temperatures was also investigated in this work. 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 (Ea) in several chemical classes of organic liquids have been obtained from Arrhenius equation plots. A strong linear relationship was found to exist between Ea and solvent molecular weight.

The maximum tangential swelling of unextracted and extracted wood of two North American wood species, sitka spruce and sugar maple, in forty organic solvents have been measured at the end of 100 days. A mild extraction with 80 % ethyl alcohol for two hours was carried out. Removal of extractives greatly enhanced the maximum wood swelling in all organic solvents used, especially in sugar maple. Rates of wood swelling of both unextracted and extracted wood in nine organic solvents have been accurately measured. Results showed that there was a significant increase in the wood swelling rate after the removal of extractives, that is, the swelling of extracted wood took place much faster and it reached an equilibrium in a shorter period of time.

Thermodynamic work of adhesion, contact angle, wettability and acid-base contributions of the wetting of four North American wood species were determined using the Wilhelmy technique (Cahn Dynamic Contact Angle Analyzer). The wetting angles with water varied from 60° for sitka spruce to 74° for Douglas-fir. Wood surfaces had a strong acidic character since the greatest interactions for all the wood species occured with formamide (basic probe) while lower interactions were obtained with ethylene glycol (acidic probe). Dispersive and polar surface free energies of wood, γ_S^d and γ_S^p respectively, were calculated using Wu's simultaneous equations. Seventy five to eighty percent of the total surface free energy of wood was due to dispersion forces. Specific wettabilities of wood, W_S, and advancing contact angles in thirty organic liquids were also evaluated. No correlations whatsoever existed between wood specific wettability and maximum tangential swelling of wood in various organic liquids.

Maximum liquid-holding capacities of various compressed fibers in water and in a series of various organic liquids have been investigated. The maximum liquid-holding capacity versus bulk density relationships gave polynomial curves with a peak. Good relative correlations for cellulose compressed fiber pellets and wood were found for the series of liquids tested. In general, liquids that swelled wood to a low to medium range (up to 6 %) did not swell appreciably α-cellulose and sulfite pulp, while good to excellent wood swelling agents swelled all the fibers very significantly. It was also found that the hydrogen bonding parameter of the swelling liquid was the most important factor. The swelling rate of various compressed fiber systems in organic liquids was dramatically increased by raising the temperature. Activation energies and molar volume of the swelling liquid were linearly correlated.

There were several questions that arose during this investigation which could be considered when planning further work in this area. The most obvious study that should be conducted concerns the effect of water on the swelling of wood in organic liquids. A series of swelling experiments should be run in order to determine the effects of water, in combination with several organic liquids, on the rate and equilibrium swelling of wood. Doping experiments could be run with addition of 1, 5, 10, 20, 50, 70 % water to the liquids. Swelling activation energies for various woods in such binary liquid systems could be obtained. The addition of water is expected to exert a dramatic influence on the wood swelling process (ie. swelling rate). Further consideration must also be given to the steric hindrance effects on the wood swelling phenomenon from solvents such as piperidine, 2, 6-dimethyl pyridine, 2-picoline, etc. Steric hindrance could be evaluated by estimating the hydrogen bonding potential of such organic solvents with methanol versus tetrahydropyran-2-methanol (THP-2-MEOH) using infrared spectroscopy technique. Another future study could be on the effect of wood porosity (along with wood density) on the rate and maximum swelling of wood in liquids. Also, the induction period may be related to wood porosity.

Additional investigation on the mechanism of swelling of wood in various decrystallizing agents such as aqueous solutions of sodium hydroxide, zinc chloride and decrystallizing solvents would provide information on the effect of crystalline swelling of cellulose in relation to wood swelling. Pyridine, which swells wood very significantly but exceptionally slowly, does not swell isolated cellulose or cellulose fibers to any appreciable extent. It may be that pyridine has a considerable effect on lignin which influences wood swelling. Therefore, evaluation of wood swelling in lignin solvents may provide valuable additional information on the role of lignin.

More analytical work on cellulose fiber swelling in organic liquids should also be carried out in the future with the use of the same LVDT. Measurements of the swelling of single cellulose fibers in various liquids with the use of a light microscope could also be carried out. This technique should provide more accurate data related to swelling of fiber cell walls. Determination of swelling of various cellulosic fibers (mechanical, thermomechanical, chemi-thermomechanical, kraft, sulfite, acetic acid, etc.) in a more extensive series of solvents and comparisons between various swellabilities of wood pulps should provide additional information on the influence of lignin and cellulose on fiber and/or wood swelling in water and organic liquids (rate, maximum extent). Also, the contribution of cell-wall restraint on the swelling of wood and the relative influence of the cell matrix (S_2 vs. S_1 or S_3) could also be obtained. Although there is very strong evidence of bonding between lignin and hemicelluloses, the question "why the cellulose/hemicelluloses/lignin matrix acts like a single polymer and shows first order reaction kinetics" remains to be answered. However, the development of a model based on the results of this study is planned for the immediate future.

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