Solubility of Structurally Complicated Materials: I. Wood

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Wood is a complex and nonuniform material. Its overall solubility is a combination of the individual components' ability to come into contact with the specified solvent (e.g., acetone) or blend. The components extracted from wood with a specified solvent represent the solubility of wood in that solvent at the condition described. Some wood compounds are soluble in water and organic solvents but the integral part of the cellular structure cannot be removed by common solvents at ambient temperature. High severities are needed for increased solubility/liquefaction due to temperature, time, and catalytic effects. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2035708]

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Contents

1. Introduction. 77
2. Theory. 78
    2.1. Composition and Structure of Wood. 78
    2.2. Principle of Solubility. 81
3. Experiment. 83
4. Results. 85
5. Comments. 90
6. Acknowledgments. 90
7. References. 91

List of Tables

1. Determination of the solubility of wood in solvents. 84
2. Amount of extractives in wood. 86
3. Selected solubility data of wood in solvents. 86
4. Conversion of wood in acidified solvents at 250 °C. 89
5. Properties of cellulose solvents. 89

1. Introduction

Large numbers of natural and synthetic substances are composed of a great number of atoms which are made of very large molecules often called macromolecules or high polymers. The structure of a macromolecule may be very complicated. For example, macromolecules in molecular biology are made of between 10 000 and 100 000 atoms and their molecular weight often exceeds several thousands. The three-dimensional arrangement of a large molecule is very complex.

The three-dimensional appearance of the matter is an apparent requirement if we examine it from microscopic or macroscopic aspects. The microstructure which depends on the nature of the atoms making up the chemical composition, governs the character of the whole material and its chemical properties.

All materials are in the solid state at room temperature (Flowers and Mendoza 1970; Shieh and Fan 1982). From their origin, they may be grouped into two categories; natural and artificial materials. Natural materials exist naturally in the surroundings without processing or human involvement. Besides rocks, a large mass of stony matter is widely used in common buildings including sandstone, limestone, slate, granite, and marble.

The biological materials are part of the living structure performing a vital function in plants, animals, and humans. Some of the important biological materials are human and animal body parts, e.g., bone, skin, internal organs, leather, fibers, silk, and wool. Wood, plant fibers, jute, cotton, flax, and rope, for example, originate from plants.

Artificial or manmade materials cover all substances which have altered microstructure as the consequence of external energy. Alloys, composites, ceramics, semiconductors, rubber, textile, and plastics belong to this category of materials.

Whether a material is useful, is cost effective, and has practical application depends on the various properties of the materials. The study of the relation between the structure and properties of materials is an important area and frequently examined by engineers and scientists. Both the macro- and microstructure of the materials play a decisive effect on the development for use in commercial products. By altering the microstructure of a material, the change in properties is carefully monitored by experiments.

The properties of matter play a significant role not only in science and technology, but in daily life. Despite their importance, many of the physical properties of commercial materials have hardly been investigated experimentally or theoretically. It is therefore worthwhile to summarize some of the

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[a)] Present address: 4, Fairways, Appleton Park, Warrington WA4 5HA, U.K.; electronic mail: ari.1@horvath.freeserve.co.uk relevant structure features and physical and chemical properties of commonest materials which have been reported so far.

There are several multivolume compilations on the properties of materials such as:

(1) International Critical Tables (Washburn, 1926–1933);
(2) Landolt-Börnstein (1976–1980);
(3) Kirk-Othmer Encyclopaedia (1964–current);
(4) Thermodynamic Research Center (Touloukian and Ho 1970–1977);
(5) DIPPR Data Compilation (1985–); and
(6) Arizona Solubility Database (Donnenfelser and Yalkowsky 1989; Yalkowsky 1991: Yalkowsky and He 2003).

These works do not provide the required solubility data for biological materials and plants.

Generally, information on the solubility of structurally complicated materials in solvents is rather scarce in the published literature. In spite of large compilations by IUPAC (IUPAC Solubility Data Project 1979–current), there is no review, assessment, or critical evaluation on the solubility of wood in organic solvents.

A comprehensive literature search revealed that there is no solubility data for two or more independent experimental determinations of the same wood specimen.

Consequently, the critical examination/evaluation of the published solubility data—as traditionally performed in the IUPAC Solubility Data Series—is not viable, since all data found are tentative. There is no choice and selection among the reported solubility data for wood specimens. This finding is quite common for structurally complicated materials, such as wood, bone, and hair, among other materials.

The purpose of the present paper is to draw together some of the recently published data concerning the solubility of wood species in organic solvents and liquids. The solubility of other structurally complicated materials, such as bone, hair, skin, and other body parts will be dealt with in subsequent papers in this series.

2. Theory

2.1. Composition and Structure of Wood

Wood is the hard tissue of the stems and branches of trees and shrubs beneath the bark. Timber is a general term applied to wood used for construction purposes. The distribution of the total worldwide wood utilization was reported by Alén (2000): fuel 50%–55%, construction 25%–30%, fiber 10%–15% and others 5%. There are great variations among different wood species. Trees may be divided into four main groups; softwoods (Gymnospermae), hardwoods (Angiospermae), food, and ornamental trees. The coniferous woods or softwoods (about 1000) are in minority relatively to the hardwoods (30 000–35 000) which grow mainly in tropical forests (Steinlin 1979).

Wood is made up of cells which contain many different polymer molecules. The wood cell contains mainly cellulose, hemicelluloses, and lignin. In addition wood contains extractives such as oils, fats, gums, and coloring matter. The content of cellulose, hemicelluloses, lignin, and extractives varies among different kinds of wood (Panshin and de Zeeuw 1980; Lewin and Goldstein 1991; Stenius 2000).

Variations exist among the different cells of diverse species and individuals as well as between different parts of the stem and within one and the same growth ring. The age of a tree can be calculated from the number of growth rings at the base of the stem. Growth conditions influence the width of the annual rings of tree species.

The transportation of water and nutrients provides the formation of the porous early wood followed by the late wood production when the growth decreases. The fibers of the late wood are denser than that of early wood. Early wood is weaker than the thick-walled late wood.

The early investigations by several workers reported that the physical properties of wood depend not only on the arrangement and size of the individual cells but also on the orientation of the spiral cellulose micelle structure of the cells composing the specimen of wood. There is a direct relationship between the length of a fiber and the angle at which the spiral cellulose micelle structure of the fiber wall is oriented with respect to the longitudinal axis of the fiber. It is possible that specimens of wood containing short fibers might possess quite different physical properties from those specimens containing long fibers.

The results obtained from several measurements indicate that the fiber length in a branch was found to be shorter than that in the trunk at the same height as the branch and the fiber length in the outer portion of a root was approximately equal to that of the outer growth rings of the trunk at the 2 ft level.

It has been found that where growth is rapid, fiber diameter is at a maximum, and where growth is slow, fiber diameter is at a minimum. Consequently, the shortest fibers have the greatest diameter and the largest fibers the smallest diameter. It is apparent that growing conditions greatly influence the character of the fibers formed.

In the case of the fiber lengths of any species of any tree, reference should be made to the actual material used and some indication given as to its position in the tree, the age of the tree, and whether considerable variation between early wood and late wood was noted. Average fiber lengths as quoted in the literature can be taken only as approximations and should be used with caution. The assessment of fiber length from samples submitted may vary from 0.6 to 1.36 mm, depending on the sampling.

Studying the fiber dimensions in several trees, it has been found that at all levels, the fiber length nearest the pith was between 0.6 and 0.7 mm, and that within 10 years, the fiber length had risen to an approximately constant value between 1.00 and 1.36 mm, depending on the level in the tree.

Vessel diameter also increases rapidly during the first 10–20 years and then tends toward a constant value. The late wood fiber length is always greater than that of the early wood.

Several physical and physicochemical properties of wood have been investigated and reported in the literature (Bisset 1951; Anonymous 1962; Overend *et al.* 1985; Fengel and Wegener 1984; Stenius 2000). These include toughness, tensile strength, hardness, permeability, shrinkage, and thermal expansion. The physical properties of wood depend on any of the following factors; cell arrangements, cell wall structure, size and type of cell contained in the specimen, the density of the specimen, its position in the tree, and on other factors including forest site and rate of growth.

Most studies focused on the possibility of establishing relationships between variations in wood structure and variations in physical properties (Oshima 1965).

Gymnosperms consist almost entirely of tracheids which are formed with their longitudinal axes in a vertical direction parallel to the pith of the tree. The tracheids are traversed at right angles by medullary ray cells whose lengths lie along horizontal lines radiating from the center of the tree. All the cells are separated from each other by a middle lamella consisting largely of lignin. Chemically gymnosperms consist of approximately 55%–60% cellulose and 25%–30% lignin. The balance is made up of resins, inclusions, and other extractives (Wise 1944; Herman 1944; Browning 1963; Rydholm 1965; Panshin and de Zeeuw 1980; Janson *et al.* 1981; Lewin and Goldstein 1991).

The micelles in the cell wall are at least 600 Å in length and 50–70 Å laterally. Cellulose consists of chains of β-glucose residues of variable length as high as 50 000 Å.

In wood fibers the micelles may be laterally separated from each other by encrusting lignin and wet wood also by water molecules which are attached to the surface of the cellulose micelles by means of hydroxyl linkages. The cell wall of a tracheide consists of a complex matrix of cellulose, lignin, and water.

Investigations found that the tensile strength of wood and other fibers is dependent on the orientation of the micelle structure of the fibers. The shrinkage of wood is largely determined by the micelle structure of its constituent fibers.

During the drying process, the change of moisture content begins to produce an appreciable effect on the particular physical properties of wood under consideration. Therefore, for most practical purposes a fiber saturation point in the vicinity of 30% moisture content is used.

Longitudinal shrinkage is only 0.1% for many timbers when dried from the green to the oven dry condition. The transverse shrinkage may be 50–100 times greater with the radial and tangential shrinkage values being 6% and 10%, respectively.

The moisture content or the fiber saturation point is expressed as the difference between the green and oven dry weight of the specimen of wood.

The basic density or specific gravity is given by the ratio of the oven dry weight of the wood specimen to the weight of water displaced by the fully water swollen wood specimen, when completely submerged in water. The basic specific gravity of timber varies between 0.20 and 1.20, but the specific gravity of dry cell wall substance is practically constant for all species with an approximate value of 1.5. This means that internal voids, containing either water or air, vary from 20% to 87% of the overall swollen volume of the wood specimen.

Compression wood differs from normal wood in that it has a higher lignin and lower cellulose content than normal wood. This may have some influence on the shrinkage.

Among the many physical and mechanical properties of wood, probably the shrinkage and thermal expansion have been studied the most. Wood is a poor heat conductor and has a low elastic modulus.

The longitudinal thermal expansion of a number of European timbers along and across the grain has been investigated. The average value of 4.7×10^{-6}/°C has been reported for timbers of elm, box, chestnut, oak, maple, spruce, walnut, poplar, fir, and mahogany. The tangential coefficient value was 45.6×10^{-6}/°C. The moisture content slightly increased the expansion coefficients.

The investigations found that the rate of radial growth affects fiber length. It follows that fiber length affects the orientation of the micelle structure of the cell walls. Consequently, the micelle orientation exerts a strong influence on the directions in which physical properties such as shrinkage, thermal expansion, and tensile strength will be most prominent.

Wood is a mixture of 40%–50% cellulose, 20%–35% hemicelluloses (polysaccharides), and 15%–30% lignin (native protolignin) together with some extractives. Cellulose exists in three forms: alpha, beta, and gamma. The Greek alphabet (alpha α, beta β, and gamma γ) is used to represent the fraction of cellulose which is soluble or insoluble in strong (17.5%) sodium hydroxide solution. This nomenclature is strictly based on separation of cellulose components by solubility. α-Cellulose is defined as the portion of the material insoluble in the sodium hydroxide solution; β-cellulose as that portion which is dissolved but reprecipitated when the solution is neutralized; and γ-cellulose as that part of the dissolved material which remains soluble in neutral or slightly acid solutions (Browning 1967). α-cellulose has the highest degree of polymerization. The β and γ forms have much lower degree of polymerization and are known as hemicelluloses.

The molecular arrangements of polymers determine the physical and physicochemical properties of wood.

Cellulose is a homopolysacharide composed of β-D-glucopyranose units which are linked together by (1–4)-glycosidic bond. Cellulose molecules are completely linear without branching and have a strong tendency to form intra- and intermolecular hydrogen bonds. The aggregated cellulose molecules form microfibrils which consist of crystalline and amorphous regions. The proportions of ordered and disordered regions of cellulose vary considerably depending on the origin of the sample (Browning 1967; Atalla 1987; Hon and Shiraishi 1991).

Cellulose is the world's most abundant and important biopolymer. Approximately 40%–50% of the dry wood consists of cellulose which is surrounded by hemicelluloses, lignin, and extractives. The cellulose molecules are in both crystalline and amorphous regions. Hemicelluloses are also amorphous, similarly to lignin.

The cellulose molecules are in a bundle and held together by hydrogen bonds. The bundles of cellulose molecules are thus aggregated together in the form of microfibrils. Microfibrils form fibrils and finally cellulose fibers. The fibrous structure and the strong hydrogen bonds in cellulose account for its high tensile strength and insolubility in most solvents. The better the solvent the more favorable the interaction with cellulose, resulting in expansion, whereas in a poor solvent the polymer is rather compact and contraction occurs.

Cellulose is distinguished analytically from the extractives by its insolubility in water and organic solvents, from the hemicelluloses by its insolubility is aqueous alkaline solutions, and from lignin by its relative resistance to oxidizing agents and susceptibility to hydrolysis by acids.

In contrast to cellulose, hemicelluloses are heterogeneous polysaccharides with a degree of polymerization of 200. They are formed through biosynthetic routes. Different monomers and side groups represent the hemicelluloses. Hemicelluloses are easily hydrolyzed by acids to their monomeric components.

The hemicelluloses content of softwoods and hardwoods are different, similar to their amount in the stem, branches, bark, and roots of the tree.

The major hemicellulose components are different in softwoods and hardwoods, as follows:

(1) Softwood: galactoglucomannan (5%–8% of wood); arabinoglucuronoxylan (7%–10% of wood); and arabinogalactan (5%–35% of wood); and
(2) Hardwood: glucuronoxylan (15%–30% of wood) and glucomannen (2%–5% of wood).

The complex lignin formula has been reported by Adler (1977). There is a large variation among the wood species. In addition, formulas for softwood and hardwood lignin have been suggested as well.

Direct ultraviolet spectrophotometric methods have been used for the determination of lignin in wood. Lignin is a polymer of phenylpropane units. Normal hardwood contains between 20% and 30%, whereas normal softwood contains 26%–32% lignin. The phenylpropane units are joined together both with C–O–C (ether) and C–C (carbon–carbon) linkages. Approximately, two thirds or more are ether type. The rest are of carbon-to-carbon type. Almost all the phenylpropane units in softwood lignin are of the guaiacyl type, but hardwood lignin contains additional syringyl units.

The structure of the lignin is rather complex due to the different types of linkages connecting the phenylpropane units, and therefore the literature should be consulted (Adler 1977). The composition of functional groups of lignin shows variations among the wood species.

The experimental difficulty in studying the macromolecular properties of lignin is the fact that lignin has a very low solubility in most solvents. Furthermore, lignin behaves quite differently in solution in comparison with cellulose.

Extractives are defined as substances present in wood, not an internal part of the cellular structure, that can be removed by solvents such as hot or cold water, benzene, alcohols, ethers, or others that do not react chemically with wood components. They are regarded as nonstructural wood constituents. Extractives contribute color, odor, and taste to wood.

Extractives are a very small fraction of wood components, usually between 3% and 5% of the dry wood weight. They comprise a large number of individual components of both lipophilic and hydrophilic types with low molecular weight.

The amount and composition of extractives differ markedly in various parts of the same tree, that is in the stem, branches, roots, bark, and needless. Phenolic compounds are in the heartwood and in bark. Resin acids are in the resin canals. Fat and waxes occupy the ray parenchyma cells.

Both softwood and hardwood contain oleoresin and parenchyma resins. Oleoresin constitutes include monoterpenoids and diterpenoids. Parenchyma resin contains triterpenoids and steroids. Some extractives constitute polyterpenes, such as rubber, gutta percha, and balaba. Terpenoids and steroids represent a wide variety of natural products with more than 7500 different structures (Stenius 2000).

Fats are glycerol esters of fatty acids occurring in wood predominantly as triglycerides. More than 30 fatty acids, both saturated and unsaturated, have been identified in softwoods and hardwoods. Waxes are esters of higher fatty alcohols (C_{18}–C_{24}), terpene alcohols, or sterols. Fats and waxes can be energy source of the biological functions in the wood cells. Resin compounds protect the wood against insect attacks.

In addition to the hydrocarbons, wood contains trace amounts of inorganic compounds and metal ions, such as iron, cobalt and manganese carbonates, silicates, oxalates, and phosphates. Their concentration seldom exceeds 1% of the dry wood weight.

Quantitative determination of extractives in wood is performed by standard methods after extraction with organic solvents, such as acetone, ethanol, hexane, diethyl ether, or dichloromethane (Holmbom and Stenius 2000).

For analytical purposes and for identification of individual components gas–liquid chromatographic methods in combination with mass spectrometry play a key role.

During the storage and seasoning of trees the content of lipophilic extractives start to decrease and their composition is changing. As the consequence of changes the yields of turpentine and tall oil decrease. Free radicals form as the result of autooxidative and enzymatic reactions.

Bark is about 10%–15% of the total weight of the dry tree. It surrounds the stem, branches, and root of the tree. The chemistry of bark is rather complicated and its composition varies among tree species and locations. Bark extractives can be divided into soluble lipophilic and hydrophilic fractions.

The extractives consist mainly of phenolic constituents. In addition to the lipophilic and hydrophilic constituents, minor quantities of soluble carbohydrates, proteins, and vitamins are present in bark.

2.2. Principle of Solubility

The thermodynamic principles of the solubility of structurally complicated materials (e.g., wood, bone, textile, etc.) in various liquids (e.g., solvents, oil, blood, saliva, mercury, etc.) have not been adequately investigated. This area of the physical chemistry has not been studied to a great extent because of the large number of variables involved.

When a solid and a solute are brought into contact with each other the attractive forces of the solvent caused by the thermal motion of the solid particles tend to break apart the structure of the solid and disperse ions or molecules from its surface. The action of the solvent is the result of the high affinity or attractive forces between the solvent and the solid particles (Horvath 1982, 1992; James 1986).

Solution is formed when the ions or molecules become dislodged from the surface of the solid into the solvent. The dispersed solid which goes into a solution is described as the solute and the process the dissolution. The ions or molecules dissolved in the solution are free to move about as a result of their kinetic energies of translation.

In the solution there is a continuous contact/return between the dissolved ions or molecules and the undissolved solid surface. When the concentration of ions or molecules becomes sufficiently high, the solution is saturated and a dynamic equilibrium will be established, then the solution is incapable of dissolving more solute particles.

The concentration of the solute in a saturated solution is termed the solubility of solute in the solvent. The solubility is dependent on the complexion of the nature of both solute and solvent and the surrounding temperature and pressure (Sedivec and Flek 1976).

The principle of the solubility of a solid material in a solvent can be divided into two major categories, that is, a reversible or regenerable and an irreversible process. In the reversible procedure, the molecular structure of the solute remains unchanged during the dissolution in the solvents. As a consequence of the unchanged structure, the solute can be recovered from the solution by unit operations, e.g., crystallization, distillation, etc.

In the case of irreversible procedure, the molecular structure of the solute changes during the solubility as a result of the interaction between the solute and solvent. Intermediate compounds are usually formed in this process. This is a very common procedure when a polymer is dissolved in strong organic solvents.

Cellulose, hemicelluloses, and lignin are polymers. In polymer solutions the movement of the large polymer molecules is restricted. This means that the entropy of mixing a polymer in a solvent is smaller than in the case of the monomer in the same solvent.

Whether a polymer will dissolve in a solvent depends on the polymer–solvent interactions and the entropy of mixing. When the molecular interactions are insignificant, then the solubility is ruled by the entropy of mixing, which is always positive. With decreasing temperature the solution separates into two phases.

If the intermolecular interactions are strong in the polymer solutions then phase separation occurs as temperature increases. The enthalpy of mixing in a polymer–solvent system governs the solubility. As the entropy of mixing becomes more negative with decreasing temperature, the solubility is more likely. Many polymer solutions phase separate when temperature increases.

The solubility of polymers decreases with increasing molecular weight.

The dissolution of cellulose is very slow due to intermediate formation of highly viscous polymer mixtures as the solvent penetrates into the polymer.

The solubility relationship between solute and solvent in a system can be greatly complicated when new compounds are formed. The new compounds are called solvates, or, if the solvent is water, hydrates (Yalkowsky and Banerjee 1992; Yalkowsky 1999). Several solvates or hydrates of different compositions may be formed by a single system. Each hydrate or solvate is stable under certain conditions of composition and temperature. Sodium carbonate forms several solid hydrates in an aqueous system.

When the solid hydrate is in equilibrium with a saturated solution of the same composition it is called the congruent point in the phase diagram. Many systems, both inorganic and organic, behave in a manner similar to that of aqueous sodium carbonate and form one or more solvates and congruent points.

In certain systems solvates are formed that are not stable and decompose before the temperature of a congruent point is reached. Such solvates undergo direct transition from the solid state into another chemical compounds. These transitions take place at sharply defined temperatures which are called transition points. There are many systems which form several solvates and show solubility relationships both with and without congruent points and transition points in the same aqueous system.

The solubility of commercial solids in organic solvents play a crucial role in their extraction chromatographic separation and reactions in solvent media. The poor solubility of many commercial solids in most organic solvents has been one of the main impediments to studying their properties. The low solubility of commercial solids in organic solvents is due to the energy required for the breaking of a large number of solvent bonds during the dissolution between the solute and the solvent. In other words, the higher or lower solubility can be explained on the basis of a better or weaker interaction between the solute and the solvent molecules.

Hildebrand's theory of regular solutions can provide a useful correlation with the solubility parameter of both the solvent and the solute (Hildebrand and Scott 1950; Barton 1991). Theory predicts that the solubility exhibits a maximum when the solubility parameter of the solvent matches that of the solute. This procedure is often applied for the calculation of the solubility parameter of a solid solute when its solubility is available in various solvents but there is no information on its heat of vaporization.

In conclusion, a solvent with a solvent parameter whose value is close to that of the solute will win over a solvent whose solvent parameter differs significantly. The experimental solubility data will aid in achieving the goal of rational choice of solvents for separation and purification of solid solutes.

However, if a polymer has a very large molecular mass (about 2 million) even the best match in solubility parameters between solvent and solute (that is polymer) will not lead to a true solution (Hansen and Björkman 1998). Nevertheless, the solubility parameter will help to interpret physical affinities phenomena, similarities, and differences in energy from a given molecular structure.

Most polymers have larger solubility parameters than those of the monomer from which they are made (Hansen 1999).

The solubility parameters alone cannot explain the results of the solvent and solute effect on wood and wood polymers. The insolubility of wood may be explained by the existence of covalent bonds between polymers in wood. The insoluble wood indicates that physicochemical phenomena other than solubility parameters have to be incorporated into the ultrastructural considerations to explain the properties and behavior of wood.

In addition to the solubility parameter, several other solvent parameters have been related direct or indirectly to the solubility. These parameters are:

(1) molecular size (molar volume),
(2) molecular surface area,
(3) polarizability,
(4) polarity, and
(5) H-bonding strength.

Several investigators showed that solvents whose n (refractive index), $\ni$ (dielectric constant), V (molar volume), and δ (Hildebrand solubility parameter) approach those of solute are relatively stronger solvents. However, the clear scatter in measured solubility plotted against any single solvent parameter indicated that although obvious trends are apparent, it is unlikely that a single universal parameter can be found for the wide range of solvents studied.

The physical and thermodynamic properties of solvents determine the magnitude of solubility or dissolution capability of various solutes. The solubility of a solid solute in a liquid solvent is a function of temperature. In addition, however, the heat of fusion of the solid solute must be considered since energy is required to overcome the intermolecular forces of the molecules in the solid while it is dissolving. The influence of the intermolecular forces upon solid solubility is manifested in the case of two chemicals of similar melting points and structure when the chemicals with higher heat of fusion have the lower solubility in any specified solvent.

The solubility of a solid solute in various solvents is largely determined by its chemical structure. As a general rule, structural similarity favors solubility. This means that the solubility of a given solid solute in a given solvent is favored if the solubility parameters of the solute and solvent are equal.

The solubility parameter of a polymer is always defined as the square root of the cohesive energy density in the amorphous state at room temperature. Beside the chemical structure the physical state of a polymer is also important for its solubility properties. Crystalline polymers are relatively insoluble and often dissolve only at temperatures slightly below their crystalline melting points. If the molecular mass of a solute increases then its solubility decreases.

The mechanism of the solubility of solid solutes in a solvent mixture has been investigated but has not been fully explained yet. The interaction between the solvent molecules in the mixture has a profound effect on the solubility which indicates the large deviation from Raoult's law.

The solvating ability of various organic solvent mixtures is different. The solvation shell is equally composed of the solvents in the mixture. Depending on the chemical environment, the lattice forces have to be overcome by the free energy of solvation to result in solubility.

Polymers are often more soluble in solvent mixtures than in pure solvents. A typical example is the solvating ability of the carbon disulphide and acetone mixture for polyvinylchloride (PVC). PVC is insoluble in pure acetone and carbon disulphide, but soluble in their mixture. Similarly, soaps dissolve in the mixture of hydrocarbon and ethylene glycol, but are insoluble in the pure solvents of ethylene glycol or hydrocarbon at room temperature. A typical commercial soap is made by reacting sodium hydroxide with a fatty acid. Solvation takes place when two different solvents in a mixture solvate the ionic and hydrocarbon ends, respectively.

The solubility of certain material in a selected solvent can be promoted by the addition of a surfactant (detergent) to the solvent. Vitamin B_{12a} (aquocobalamin) is insoluble in benzene. However, the presence of surfactant (dodecylammonium propionate) will solubilize the large molecule.

Data presently available in the literature limit the strict applicability of the methods described for the estimation of the solid solubility in various solvents. The expressions reported and reviewed in the publications (e.g., Lyman *et al.* 1982; David and Misra 1999) are applied to pure chemicals with well defined chemical structures. Such properties as the melting point and heat of fusion of the solid solute are available or can be estimated or experimentally determined. However, commercial solids like wood, bone, food, etc., consist of a mixture of different often large molecules, without measurable T_m and ΔH_f, which are required to overcome the intermolecular forces of the molecules in the solid while it is dissolving.

Isolated constituents do not represent their natural state in the wood structure, but can give indications on possible conformations. Lignin and hemicellulose molecules can form complexes which may be inseparable in the native state without having formed covalent bonds. In addition to the temperature and pressure dependence of the solid solubility in liquids, the solubility also depends upon the particle size as the earlier investigators reported (Hulett 1901; Dundon and Mack 1923; Cohen and Thönnessen 1932; Hildebrand and Scott 1950). The particle size dependence of the solubility in the solute–solvent system is expressed by Guggenheim (1952):

$$RT\log_{10}(f^l/f^s)=\frac{2V\gamma}{r}$$

where f^l = fugacity of the solvent (liquid); f^s = fugacity of the solid (solute); V = molar volume of the solvent; γ = surface tension of the solvent; and r = radius of the dispersed solid particle.

Several more recent studies have been reported on the effect of particle sizes in solubility determinations (Pedersen and Brown 1976; Fürer and Geiger 1977; Kaneniwa and Watari 1978; Kaneniwa *et al.* 1978; Morokhov *et al.* 1979; Yu 1982).

The effect of particle size on solubility is a result of surface energy effects similar to the enhancement of vapor pressure over small drops.

The pretreatment of the samples, especially grinding and drying, can substantially influence the solvent penetration, and thus the extraction/solubility efficiency.

The solubility of solid material is increased with increase in its degree of subdivision. This increasing solubility with diminishing particle size is demonstrated by the behavior of crystals that are in equilibrium with their saturated solutions. Where such an equilibrium exists, the total amounts of solid and liquid must remain unchanged. However, the equilibrium is dynamic, resulting from equality between the rates of dissolution and crystallization. As a result of the effect of particle size on solubility, the small crystals in such a solution will possess higher solution pressure than the larger ones and will tend to disappear with corresponding increase in size of the large crystal. This growth of large crystals at the expense of small ones in a saturated solution is a familiar phenomenon of considerable industrial importance. For the same reasons, an irregular crystalline mass will change its shape in a saturated solution.

In theory the solubility of very small particles is higher than that for larger particles of the same material and in the same solvent. It can be shown that in the general case the following relationship is applied (see e.g., Modell and Reid 1974):

$$S_s=S_i\exp\left(\frac{2\sigma V^s}{RTr}\right)$$

where S_s = solubility of small fine solid particles; S_i = solubility of large identical solid particles; σ = solid–liquid interfacial tension; V^s = molar volume of the solid at T temperature; and r = radius of spherical solid particles.

However, the reliability of the above expression has been criticized by Harbury (1946) and later investigators:

(1) The solid particles are not spherical and the radius (r) does not represent the geometric shape of the solid.
(2) The solid–liquid interfacial tension (σ) does not give a realistic value for highly diluted solutions.
(3) The activity cannot be substituted by concentration for highly concentrated solutions, that is, when the solubility is high.

In practice the solubility difference between small and large particles is more convincing when the small particles are in the 10–100 Å range and a correction factor is applied instead of the interfacial tension (σ).

The reduction of large pieces of solids to smaller size or powders by grinding or dispersion is required by enhancing the completeness and rapidity of the solubility in solvents. The production of the surface within maximum and minimum size limits may be important.

There are several factors that affect the grinding characteristics of a material, such as structure, hardness, and water content. The material can be hygroscopic, has a tendency to flocculate and agglomerate, and is sensitive to temperature changes. Resins and gums become soft and plastic beyond a critical temperature; other solids may burn or char; certain chemicals and dyestuffs are unstable and may ignite or explode if the temperature is excessive; and some mineral pigments such as ochres and siennas tend to change in color at elevated temperatures or under mechanical action.

3. Experiment

The experimental determination of the solubility of solid materials can only be as good as the preparation used for sampling the test specimens. Unlike gases and liquids, the properties of dry powders are sensitive to a size distribution which affects the solid solubility. The representative sampling is absolutely critical for the reliable solubility measurements. The objective of the sampling is to assemble a sample which is representative of the total dry mass of material from which it was taken. This can be achieved by taking many small samples from all parts of the total with an acceptable degree of accuracy. By this way all dry particles in the total must have the same probability of being included in the final sample.

Particle size and shape affect the solubility of solid materials. Flaky or stringy particles like sawdust, mica or asbestos, and textile fibers are difficult to handle because they interlock. In many cases, particle size and shape do not exist independently and shape can be size dependent. Frequently used shape factors are: sphericity, circularity, surface-shape coefficient, volume-shape coefficient, and surface-volume shape coefficient.

An irregular particle can be described by a number of sizes, such as the equivalent sphere diameters, the equivalent circle diameters, and the statistical diameters.

When selecting a method, it is best to take one that measures the type of size which is most relevant to the solubility which is under study. It is the surface-volume diameter which is most relevant to the solubility determination.

Powders or any dry particulate materials can be classified into different categories according to their handling properties. The classification depends on the type of handling in question, there are at least three such types: (1) handling and storage of de-aerated powders, (2) handling of aerated powders, and (3) pneumatic conveying.

The specific surface area of the solids is an important characteristic in applications where the process is surface dependent like in solubility, activity of drugs, etc. This is a measure of the fineness of the particles as well as of their porosity. The specific surface area increases with decreasing particle size. For further discussions, the reader is referred to several publications on the subject (British Standards 1971; Sing 1976; Gy 1982; Beddow 1984).

Samples of wood originating from different trees or even from different locations in the same tree may vary considerably in anatomical structure and in physical, chemical, and mechanical properties (Smook 1992; Biermann 1993, 1996).

The constituents and composition of wood are rather complicated and vary considerably depending on the morphological origin and the age of the sample. The structure of wood contains homopoly saccharides, heterogeneous polysaccharides, polymers of phenylpropane, etc.

There are great differences among the various wood cell types in hardwood and softwood. One of the important chemical differences, both qualitatively and quantitatively, is in their lignins. Softwood lignin is derived from phenyl propane units carrying one methoxyl group and constitutes 24%–33% of the wood. Hardwood lignin is derived from phenyl propane groups carrying two methoxyls and constitutes only 19%–28% of the wood.

The hemicellulose content of softwood and hardwood is chemically different. In softwoods there are 7%–14% xylan and 12%–18% galactoglucomannan. In hardwoods there are 19%–26% hardwood xylan.

Sampling wood is subject to many variations. It is important that samples are carefully defined according to species, site, age, date, condition, and vertical and horizontal location, etc. within the tree. The chemical composition among trees and even within the same tree varies.

The list outlined in Table 1 is based on sampling techniques developed by wood chemists and technologists during the past 2 decades. For more details it is recommended that the reader consults several textbooks on analytical wood chemistry (Sjöström *et al.* 1966; Sjöström and Alen 1991; Sjöström 1993; Holmbom and Stenius 2000).

Samples of the solvents may be purchased and purified in the laboratory when necessary. The purity can be checked by melting-temperature measurements, by low-temperature calorimetry, or by gas chromatography (Reichardt 1988; Grant and Higuchi 1990; Ash and Ash 1996; Lide 1996; Marcus 1998).

Before use, the solvent samples are dried in the vapor phase by passage through a column, 15 mm in diameter and 30 cm long, containing molecular sieve 5A which had been activated at 200 °C for some hours in a current of air.

TABLE 1. Determination of the solubility of wood in solvents

1. Origin of wood
    - Location
    - type of tree
    - age and height
    - position of the cutting/sawing
    - number of rings used, counted from the core
2. Preparation
    - sawdust with 10–100 μm average size
    - seasoning in an oven at 80 °C for 5 days
    - cooling in a desiccator for 24 h
    - weighing the samples on an analytical balance
3. Source and purity of the solvent
    - name and address of manufacturers
    - purity and impurities stated
    - HPLC- or AR-grade solvents were used for the measurements
    - was the solvent purified by chromatography?
4. Experimental proceeding
    - mixing the solvent with the sample in a stoppered Erlenmeyer flask
    - mixture was agitated by a magnetic stirrer for 5 days at room temperature
    - after agitation the sediment has been separated by filtration using a glass filter
    - residue was washed with pure solvent and dried in an oven at 100 °C keeping the sample in a desiccator overnight
5. Evaluation of the results
    - weighing of the dry residue on an analytical balance
    - difference between the weights of the original sample and the dry residue has been calculated and the solubility is expressed in percent by weight

Some higher molecular weight solvents form a low-boiling azeotrope with water and therefore are dried by distillation of a small fraction from the ebulliometer before the start of measurements.

Several series of measurements are made with fresh samples because the scatter of the results is larger than had normally been obtained for a stable substance at relatively low temperatures. For instance, the values for the solubility obtained with three different samples from one batch of material range from 0.10 to 0.12 g/L. The lack of precision appeared to be due to the difficulty of removing water from the solvent and the measurements were made on a sample which had been allowed to stand for some weeks over calcium hydroxide in a bulb attached to the apparatus so that the solvent could be transferred to the boiler without exposure to the atmosphere.

After careful treatment of the sample material, the test specimen of known mass is immersed in the solvent under specified conditions of time, temperature, and volume. The determination of the loss in mass is the difference in the mass of the dry sample before and after treatment. The flask containing the sample and the solvent is shaken gently to ensure complete wetting of the test specimen. It was further shaken gently for several hours and then the contents were transferred to a glass filtering crucible. The residue in the crucible is washed and drained by suction. After drying the residue in an oven, it was cooled in a desiccator and the mass was determined.

The solubility of the material in solvent S, as the loss in mass of the test specimen is expressed as a percentage of it calculated dry mass, is given by the formula

$$S(\%)=\left(\frac{m_1-m_2}{m_1}\right)\times 100,$$

where m_1 is the dry mass of the test specimen (g) and m_2 is the dry mass of the residue (g).

Measurements on some samples had to be terminated because of the onset of decomposition, apparent from the unsteadiness of the temperature readings. One or two of the measured points for each of these compounds were later discarded because of their inconsistency with the equations fitted.

If a sample used was of relatively low purity, this was acceptable because decomposition rather than lack of purity is the condition limiting the accuracy of measurements.

4. Results

Because of the complicated molecular structure of wood, its solubility mechanism in aqueous and organic solvents departs from that of a pure solute. The multicomponent composition of the wide variety of wood is often treated with various solvents for extracting one or several useful chemicals. In addition to solubilization there are several wood processing operations at various temperatures and pressures, such as solvent extraction, solvolysis, hydrolysis, solubilization, fractionation, liquefaction, partitioning, leaching, saponification, emulsification, pulping, cooking, and percolation.

Most of the nonstructural wood constituents can be removed by extraction with suitable solvents, such as water, acetone, benzene, ether, ethanol, dichloromethane, methanol, hexane, toluene, tetrahydrofuran, and petrol ether. These solvents can be divided into hydrophilic (acetone, ethanol) and lipophilic (benzene, ether, petrol ether) compounds. According to the different solubilities of the extractives many extraction schemes and sequences have been reviewed by Browning (1963).

Dichloromethane is a good solvent, but has health and environmental hazards. Acetone is inert and stable and is not harmful from the points of view mentioned (Holmbom 1999). Acetone can provide complete extraction of wood resin components, but it also extracts some other wood chemicals such as various salts, phenolic compounds, and sugars. Limited extraction has been found of hemicelluloses and pectic compounds.

Nonpolar solvents, such as alkanes, selectively extract lipophilic wood resin components, but do not always give complete extraction. Moderately polar solvents, e.g., aromatic hydrocarbons, ether, chloroform, and dichloromethane will extract polar components and some wood resins. Benzene as a solvent has been replaced by more environmentally friendly compounds, such as cyclohexane or toluene, often in combination with ethanol (2:1 portion).

Generally, wood does not contain many water-soluble organic compounds, even if high amounts of tannins and arabinogalactans are present in some species. Tannins are soluble in hot water and some polyoses such as arabinogalactans from larch species and some hardwood polyoses are also water soluble. The main components of the water-soluble part of wood consist of carbohydrates, proteins, and inorganic salts. Water removes the inorganic compounds from wood by an extraction step.

Fatty acids, resin acids, waxes, tannins, and coloring matter are the most important substances extractable by solvents.

Soxhlet, Soxtec extractors, and accelerated solvent extraction (ASE) techniques are used for extraction of wood grounded to at least 40 mesh (TAPPI 1987, 1988; Sitholë *et al.* 1991).

The extractive content of 97 commercial timbers was compiled by Dietrichs (1972). Most of the data are based on a dissertation by Puth (1964).

Often the solvent mixtures produce better results than the pure solvent alone. The following solvent mixtures have been introduced with better yield; acetone–water (9:1) ethanol–toluene (1:2), acetone–hexane, and ethanol–benzene (1:2). Each solvent or solvent mixture has its advantage or disadvantage for extraction of wood (Yu 1982; TAPPI 1987).

The amount of extractives constitutes 1%–5% of the dry wood. However, some trees can have up to 30% tannins and larches.

The chemical composition of extractives is very complicated. Several hundreds have been identified in many different wood species (Hafizoglu 1987; Stenius 2000; Balaban and Uçar 2001a; Uçar & Balaban, 2002).

Wood extractives can be divided into two major groups according to their solubility in water or organic solvents at ambient temperature. At higher temperatures the separation between water-soluble and organic solvent extractives diminishes. When the temperature rises to the supercritical condition, then all the extractives together with cellulose components become soluble in water.

The water-insoluble components are nonpolar compounds and often called wood resin, wood petch, or lipophilic extractives.

Wood resin components can be extracted with acetone but it dissolves other components too. Alkanes dissolve lipophilic extractives, but the result does not produce a complete extraction. The polar components of wood are often extracted with chloroform, ethers, dichloromethane, or aromatic hydrocarbons.

Extractives represent only a small portion of wood, but include a large number of various organic and inorganic compounds. The great number of extractives can be classified according to their metabolic processes (Theander 1985), shape of structures, solvating ability, etc. (Stenius 2000). The lipophilic extractives are divided in aliphatic components (alkanes, alcohols, acids, fats, waxes), terpenoids and steroids, phenols, and tropolones (Theander 1985). The phenolic components and tropolones are soluble in nonpolar solvents. The total amount of extractives in three wood species is given in Table 2

TABLE 2. Amount of extractives in wood

Wood species	Common name	Percent of wood dry solids (%)
Pinus sylvestris	Scots pine	2.5–4.5
Pices abies	Norway spruce	1.0–2.0
Betula pendula	Silver birch	1.0–3.5

The components extracted from wood with a specified solvent represent the solubility of wood in that solvent at the condition described. In the Soxtec and Soxhlet systems the temperature corresponds to the boiling point of the solvent. The solubility data presented in Table 3 are a collection from selected sources.

The chemical composition of the wood extractives includes phenolic constituents, fats, waxes, stereoids, and terpenoids. Most of these chemicals are lipophilic and soluble in organic solvents. Triterpenoids and steroids occur in fatty acids esters (waxes) and they are sparingly soluble hydrophobic compounds. Examples of common terpenes and terpenoids are listed by Alén (2000). In addition there are also water soluble (hydrophilic) components, such as carbohydrates and inorganic substances in wood.

Due to the presence of a large number of organic compounds (several thousands of individual chemicals) in the extractives (nonstructural wood constituents), the following techniques are used for determination of components: gas chromatography, high-performance liquid chromatography, size-exclusion chromatography, supercritical fluid chromatography, and thin-layer chromatography. Direct spectroscopic analysis using nuclear magnetic resonance or infrared spectroscopy is in development.

Wood resin is a water-insoluble extractive and soluble in neutral solvents with intermediate polarity, such as hydrocarbon solvents, ethers, and chlorinated methanes. Both softwoods and hardwoods contain resin acids, steryl esters, diterpenoids, and fats.

The lipophilic constituents can be extracted with nonpolar solvents, such as diethyl ether, dichloromethane, chloroform, aromatic hydrocarbons, etc., but do not always give complete extraction. The hydrophilic fraction is extractable with polar organic solvents, such as ethanol, acetone, etc., and water.

Gums represent water-soluble wood polysaccharides and they are classified according to their shape, e.g., linear, branched, etc. Some trees exude gums as viscous fluids. They are known as gum arabics, gum karaya, etc. Gums are tasteless, odorless, colorless, and nontoxic.

In addition to lipophilic and hydrophilic constituents, minor quantities of soluble carbohydrates, proteins, vitamins, starch, pectins, and oligosaccharides are present in bark. The insoluble constituents of bark are polysaccharides, lignin, suberins, and inorganic solids, such as oxalates, phosphates,

TABLE 3. Selected solubility data of wood in solvents

Wood species	Solvents	Solubility (wt %)	References
Pinus brutia	Water	1.54	Balaban & Ucar (2001a)
Pinus nigra	Water	4.18	Balaban & Ucar (2001a)
Fagus orientalis	Water	2.34	Balaban & Ucar (2001a)
Fagus sylvatica	Water	3.36	Balaban & Ucar (2001a)
Fagus orientalis	Ethanol	0.45	Balaban (2000)
Pinus brutia	Ethanol	0.25	Balaban (2000)
Pinus sylvestris	Ethanol	0.17	Balaban (2000)
Quercus vulcanica	Cyclohexane	0.22	Balaban & Ucar (2001b)
Juniperus excelsa	Cyclohexane	0.3	Balaban (1997)
Juniperus foetidissima	Cyclohexane	1.58	Balaban (1997)
Pinus nigra	Cyclohexane	5.1	Ucar & Balaban (2002)
Cedrus libani	Ethanol	0.2	Brasch & Jones (1959)
	Cold water	0.8	Brasch & Jones (1959)
Cedrus penhallowii	Ethanol	0.3	Brasch & Jones (1959)
	Cold water	3.3	Brasch & Jones (1959)
Picea excelsa (spruce)	Acetone	2.2	Assarsson & Åkerlund (1966)
	Ethyl ether	1.24	Assarsson & Åkerlund (1966)
	Petroleum ether	1.04	Assarsson & Åkerlund (1966)
Pinus silvestris (pine)	Acetone	3.10	Assarsson & Åkerlund (1966)
	Ethyl ether	2.42	Assarsson & Åkerlund (1966)
	Petroleum ether	2.29	Assarsson & Åkerlund (1966)
Betul verrucosa (birch)	Acetone	3.46	Assarsson & Åkerlund (1966)
	Ethyl ether	2.03	Assarsson & Åkerlund (1966)
	Petroleum ether	2.03	Assarsson & Åkerlund (1966)
Populus tremula (aspen)	Acetone	4.53	Assarsson & Åkerlund (1966)
	Ethyl ether	2.30	Assarsson & Åkerlund (1966)
	Petroleum ether	2.27	Assarsson & Åkerlund (1966)
	Dichloromethane	1.24	Sitholë *et al.* (1991)
Populus deltoids	Ethanol	2.2	Heitz *et al.* (1994)

silicates, etc. However, some of the metal salts are sparingly soluble.

The choice of solvent is a compromise among solvent selectivity, solvent capacity, toxicological considerations, system physical properties, and solvent recovery difficulties. However, the selection of the most appropriate solvent will thus be dominated by the balance between solvent selectivity and capacity.

The first criterion for selecting a solvent or solvent blend is its capacity to dissolve the solid material. Because of the numerous materials and solvents available, the selection of the solvent is best carried out with the aid of a computer program.

Low molecular volume esters, ketones, and ethers have solubility parameters which have an energy level too low to dissolve lignin. However, N-methyl morpholine-N-oxide (MMNO) dissolves lignin at room temperature. Further solvents as dimethyl sulfoxide and N,N-dimethyl acetamide (DMAA) containing 8% lithium chloride are discussed in connection with wood solubility (Hansen and Björkman 1998). Pure dimethyl sulfoxide (DMSO) can only swell amorphous cellulose while MMNO dissolves this polymer. Both DMAA and MMNO solvents act very differently for all three wood polymers.

No simple solvents for cellulose have so far been found at ambient temperature. All known solvents for unsubstituted cellulose are of multicomponent composition (Valtasaari 1971). However, there are several metal chelate solvents: cadoxen (Cd–ethylenediamine), CuEn (cupriethylene diamine), EWNN or FeTNa (iron–sodium–tartrate), and CuAm (cupriammoniumhydroxide) which have been studied as cellulose solvents.

CuAm and CuEn have the disadvantage that the dissolved cellulose is sensitive to degradation by atmospheric oxygen in the strong alkaline copper solutions. Both cadoxen and FeTNa complexes produce stable solutions of cellulose that are only slightly subject to oxidation (Browning 1967). CuAm dissolves cellulose with the formation of a complex which has been formulated as $[\mathrm{Cu(NH_3)_4}]^{2+}2[\mathrm{Cu(C_6H_7O_5)}]^-$. CuEn dissolves cellulose as the complex $[\mathrm{Cu(en)_2}]^{2+}2[\mathrm{Cu(C_6H_7O_5)}]^-$ where (en) represents ethylene diamine. The EWNN solvent has proved a very valuable means for cellulose characterization (Schurz 1977).

Cellulose is soluble only in strongly alkaline solutions of certain metal complexes, such as the amine and ene complex bases of cobalt. After the introduction of a cobalt ethylene diamine complex for cellulose, several other metal complexes have been proposed with similar dissolving power; Cd, Cu, Fe, Ni, and Zn, see Table 5 (Jayme 1978).

Cadoxen [tris(ethylenediamine) cadmium dihydroxide] is a colorless solvent which dissolves high molecular weight cellulose ($\mathrm{MWt}>10^6$). The solubility of cellulose in cadoxen depends on complex formation involving the C-2 and C-3 hydroxyl of glucose residues. Dissolution of cellulose is essentially due to an acid–base reaction between the polysaccharide (cellulose) and the base in cadoxen.

A possible explanation for the individual behavior of cellulose in the complex solutions might be attributed to the effect of binding the metal to cellulose on dissolution. The bulky base cations ($\mathrm{Cd\,en_3^{2+}}$) enter the cellulose structure and cause it to swell and eventually dissolve. Probably even ethylene diamine takes an active part in the dissolution process (Vink 1964). A similar situation is also encountered with some other metal–base cellulose solvents (Cooxen, Nioxen, and Zinkoxen) where an excessive en concentration in general increases the solvating power of the solvent.

The solubility and regeneration of cellulose in various solvents have been investigated by Guthrie and Hardcastle (1977). The solvents used included dimethyl sulfoxide, dimethylformamide, pyridine, and tetrahydrofuran. The setup consisted of a flask equipped with a condenser, drying tubes, and a stirrer. In the system 1 g of cellulose was dispersed in 100 g solvent and heated to the reflux temperature (280 °C for dimethyl sulfoxide; 152 °C for dimethylformamide; 115 °C for pyridine; and 65 °C for tetrahydrofuran). A clear solution was obtained after 15 h for dimethyl sulfoxide; however, for the other three solvents no solution was apparent and the product appeared as a finely divided mass.

The chemical nature of the DMSO/PF system has been studied by Johnson and co-workers (Johnson *et al.* 1976). The total solution of cellulose has been accomplished with the DMSO/PF system in a variety of ways. Dimethyl sulfoxide countering 0.5% of dissolved paraformaldehyde has been found to be an excellent nondegrading solvent for cellulose at 130 °C. A similar experiment has been performed by Swenson (1976) at 128 °C. The cellulose has been regenerated from DMSO/PF solution by dilution with either water or methanol. The mechanism by which cellulose dissolves in the DMSO/PF system is dependent on the formation of methylol cellulose.

If nitrogen tetroxide ($\mathrm{N_2O_4}$) or nitrosyl chloride is introduced into dimethylformamide (DMF) or dimethylacetamide (DMAC), a certain amount of cellulose dissolves readily in these mixtures (Schweiger 1974). The viscous solutions become greenish blue from $\mathrm{N_2O_4}$ and reddish brown color from NOCl. With an increase of the $\mathrm{N_2O_4}$ or NOCl amounts relatively to cellulose, clear solutions have been obtained at room temperature. The significance of the dissolution process was that cellulose can be regenerated from these clear solutions by contact with water or with simple alcohols, e.g., methanol or ethanol. The examination by infrared spectroscopy showed that the regenerated cellulose was chemically unmodified. Furthermore, there was no indication for depolymerization, checked by viscosity measurement. The various methods used for the cellulose samples showed that the starting material was identical to the regenerated material. However, the experiments concluded that the treatment of cellulose with $\mathrm{N_2O_4}$ in other solvents, such as $\mathrm{CCl_4}$, usually results in oxidation (Schweiger 1969).

It is a well established fact that the dissolution of cellulose in effective solvents depends on the degree of polymerization of cellulose. Okajima (1978) found that a mixture of DMSO/chloral/triethylamine is a very effective solvent mixture for cellulose at room temperature. A low level of triethylamine acts as a dissolving catalyst. In the salvation mechanism cellulose goes through cellulose monochlorate formation at the C-6 position. No polymer degradation was observed.

Cellulose can be dissolved in hydrazine at high temperature (170 °C) under endogenous pressure for 1 h (Kolpak *et al.* 1977).

The effect of various solvents on the solvolysis of wood (Eucalyptus) has been studied by Heitz *et al.* (1988) as a function of the severity parameter R_0:

$$R_0 = t \exp\left[\frac{T-100}{14.75}\right],$$

where t is the time in minutes and T is the temperature in °C.

Hemicelluloses, lignin, and extractives are solubilized at $\log R_0 < 5.2$ in methanol and ethylene glycol, but the residue consists of cellulose which requires higher severities to induce solubilization. Ethylene glycol, guaiacol, cresols, and phenol behave very similarly toward solubilization of hemicelluloses and lignin without altering the cellulosic matrix.

Water and simple alcohols are not selective, resulting in char formation with increasing severities.

The solubility of eight softwoods and ten hardwoods in hot water and 1% NaOH solution has been studied by Balaban and Ucar (2001b). The investigation focused on the acidity of wood which arose from the hydronium ions released by free and bound organic acids present in extractives and noncellulosic polysaccharides and also by simple phenols, complex polyphenols, and tannins.

The dissolution, solvolysis, and liquefaction of wood and biomass are various processes to produce either valuable chemicals or stable liquid fuels. The first experimental setup was reported in the 1970s. The dissolution of wood was performed in various alcohols.

It has been known for a long time that aliphatic alcohols (C_1-C_7) or polyols dissolve selectively the basic components of wood: holocellulose and lignin.

The total dissolution or liquefaction of wood with neutral solvents is rather slow and ruled by pyrolysis producing residual solid, that is coke from the degradation products of wood. The production of coke is promoted not only by the acidity of the solution but also by the temperature rise.

Most of the investigations in wood dissolution/liquefaction have been carried out only at bench scale. In addition to the simple aliphatic alcohols several other solvents have been tested by Yu (1982), Heitz *et al.* (1994), and Rezzoug and Capart (1996). These solvents included phenol, cresol, guaiacol, acetone, ethylene glycol, lactic acid, and ethanolamines. In most cases the solvents contained a small amount of sulfuric acid (up to 1%) which favors hydrolytic cleavages along the cellulosic chain.

The basic components of wood, hollocellulose and lignin, are soluble in neutral solvents but cellulose requires solvolytic power via catalysis by acids and bases at higher temperatures in the range of 250–350 °C.

Yu (1982) reported the total dissolution of wood with a mass ratio of 4/1 ethylene glycol–wood mixture at 350 °C. An addition of a small amount of H_2SO_4 enhances the dissolution at a lower temperature. The dissolution power of several solvents has been classified by Yu (1982) according to their pK values. Alcohols with higher molecular weights are better solvents for wood than the simple aliphatic alcohols, e.g., methanol, ethanol, propanol, etc.

The solubility of wood in organic solvents has usually been investigated in an attempt to gain some insight into the complex mechanisms that are involved in wood liquefaction. The direct liquefaction of wood (Pinus radiata) occurs in the presence of an organic solvent (e.g., tetralin) at high temperature (about 400 °C) and moderate H_2 or N_2 pressure with or without catalyst (Araya *et al.* 1986). The early organosolve pulping of wood has been studied by Aronovsky and Gortner (1936) using alcoholic solvents. During the later years the supercritical gas extraction technology has been developed for wood liquefaction (Labrecque *et al.* 1984; Taylor 1996; Sun 2002).

Heitz *et al.* (1994) treated wood (Populus deltoides) with straight chain alcohols from methanol to n-hexanol, water, acetone, cyclohexane, ethylene glycol, mono- and triethanolamine, and lactic acid to test the liquefaction mechanisms where temperature and time trigger the bond rupture with or without the interaction of the solvents. The results clearly suggest that basic and acid solvents show a significant effect in liquefaction that catalysis is involved in the process. Via catalysis by acids or bases no significant residual char is produced and the lignocellulosic matrix is entirely liquefied. Cellulose, hemicelluloses, and lignin are solubilized cocurrently mainly due to nonselective extensive solvolysis at temperatures beyond 230 °C.

The direct wood liquefaction of pure sawdust (Pinus radiata) in a hydrogen donor solvent (tetralin) using various catalysts at hydrogen pressure and 400 °C was studied by Araya *et al.* (1986). Among the various processes under study for the solubility/liquefaction of wood and biomass are the supercritical gas extraction (Labrecque *et al.* 1984; Taylor 1996; Sun 2002), organosolve process (Aronovsky and Gortner 1936), and thermochemical liquefaction (Panshin and de Zeeuw 1980).

Rezzoug and Capart (1996) also investigated the classification of acidified solvents and found that the classification agrees with that of Yu (1982). The results indicate that the same classification is valid for pure solvents too. The wood dissolution in acidified solvents is graphically illustrated by Rezzoug and Capart between 175 and 300 °C. The maximal solubility of wood in most acidified solvents was found at about 250 °C during 30 min reaction time. The conversion of wood in various acidified solvents is shown in Table 4.

The solubility curves illustrate that phenol is the best solvent for wood among the tested solvents at the same condition. However, phenol condenses with the degradation products of wood. A 50/50 phenol–tetralin mixture is a good compromise for obtaining a complete conversion of wood with relatively low oxygen content of the solvolytic oil.

TABLE 4. Conversion of wood in acidified solvents at 250 °C

Solvents	Solubility parameter $(\mathrm{cal/cm^3})^{1/2}$	Conversion (%)
Phenol	12.1	100
Ethylene glycol	9.1	98
Butanol	11.4	90
Propanol	11.5	76
Ethanol	12.7	64
Methanol	14.3	58
Tetralin	9.5	44

Sorption, swelling of amorphous and crystalline cellulose, and solubility are related to the degree of reaction between the polymer and solvent. How effective a solvent is on cellulose depends on the hydrogen-bonding strength and molecular size. Limited swelling of the amorphous cellulose does not cause intercrystalline swelling. The swelling will increase by more effective solvents whose hydrogen-bonding strength permits the penetration into the tightly bonded regions of amorphous cellulose. However, the molecular size can control the number of molecules entering the available sites, that is large molecules decrease swelling. The hydrogen-bonding capacity of the solvent could be correlated with the reciprocal of the solvent molecular size.

Among the basic structural components of wood (cellulose, hemicelluloses, and lignin) cellulose shows the greatest resistance against organic solvents at ambient temperature. If a solvent dissolves cellulose, then it is most likely that it also dissolves hemicelluloses and lignin.

Lignin is chemically linked to at least part of the wood hemicelluloses, although there are even indications of lignin and cellulose bonds.

For penetrating the cellulose crystallites, very strong hydrogen-bonding solvent with small molecular volume such as lower aliphatic primary amine is required or a strong base to produce ionization of the cellulosic hydroxyls. The extent of swelling is determined by the solvated counterion and if the swelling is extensive then the separation of the polymer chains can take place and a solution is formed. This is due to the fact that the strong solvent is able to penetrate the crystal lattice of cellulose (Schuerch 1965).

Cellulose can be directly dissolved in concentrated acids, e.g., phosphoric acid and trifluoroacetic acid. However, the dissolution leads to a hydrolytic cleavage of the cellulose chains and the cellulose molecules are transformed to derivatives, such as esters.

The swelling of cellulose in organic solvent is related to the swelling of wood. The swelling of the cellulose appears intercrystalline (the solvent enters into the amorphous areas) and intracrystalline (the solvent penetrates in the crystalline regions). Limited swelling occurs when the solvent affects the interfibrillar bonding and the cellulose partially reacts with the solvent. The solvent forms complexes with the cellulose when unlimited swelling arises as a consequence of breaking the adjacent bonds. The resulting separation of the polymer chains indicates the beginning of the solubility.

In wood a cellulose molecule has a hydrophobic character due to intermolecular hydrogen bonds, but the molecules normally form crystalline regions. The presence of crystallinity has an effect which may be compared with that of crosslinking between molecules or very large molecular mass.

In the presence of oxygen cellulose depolymerizes in both Schweizer's and CED solutions. However, cellulose shows a good stability in the transparent Cadoxen and EWNN (see Table 5).

Cellulose swells in different solvents, e.g., acids and salt solutions. The extent of swelling depends on the solvent as well as on the nature of the cellulose sample. The better the solvent the more the polymer swells, whereas in a poor solvent contraction occurs.

The chemical and physical properties of cellulose are usually studied in solutions, using solvents such as CED and Cadoxen (Brown 1967). Their dissolving ability entails formation of a complex with the two secondary hydroxyl groups in cellulose and with breaking of hydrogen bonds.

Hemicelluloses consist of extensively branched polysaccharides. Fragment of hardwood xylan and the arabinoglactan are readily soluble in water. Certain tropical trees exudate gums which are rich in polysaccharides and are water soluble, e.g., gum arabic.

Hemicelluloses can be isolated from wood or pulp by extraction with neutral solvents such as dimethyl sulfoxide. The extraction is not completed but the advantage of the solvent is that no chemical change takes place in the solution. More xylan can be extracted with alkali (NaOH or KOH), but the alkali extractions have the disadvantage of deacetylating the hemicelluloses almost completely.

TABLE 5. Properties of cellulose solvents

Number	Solvents	Chemical formula	Properties
1	Cadmium ethylenediamine hydroxide (Cadoxen)	$\mathrm{Cd(CH_2[NH_2]{-}CH_2[NH_2])_3(OH)_2}$	Colorless cellulose solvent
2	Cupriethylene diamine hydroxide (Cuen, CED, Cuprien)	$\mathrm{Cu(CH_2[NH_2]{-}CH_2[NH_2])_2(OH)_2}$	Purple liquid; dissolves cellulose products
3	Schweizer's solution (Cuoxam, Cupram, Cuam)	$\mathrm{[Cu(NH_3)_4](OH)_2}$	Solution of $\mathrm{Cu(OH)_2}$ in strong $\mathrm{NH_3}$; blue liquid; dissolves cotton, silk, and linen
4	Iron–sodium tartrate complex (EWNN)	$\mathrm{[Fe(C_4H_3O_6)_3Na_6]}$	Green and odorless solution
5	Cooxene	$\mathrm{Co(CH_2[NH_2]{-}CH_2[NH_2])_3(OH)_2}$	Red viscous solution
6	Nioxene	$\mathrm{Ni(CH_2[NH_2]{-}CH_2[NH_2])_3(OH)_2}$	Violet viscous solution
7	Zincoxene	$\mathrm{Zn(CH_2[NH_2]{-}CH_2[NH_2])_3(OH)_2}$	Colorless solution

The extraction of lignin from wood is performed after hydrolysis with sulfuric or other acids. After the hydrolysis structural changes in the lignins are possible. From the solution lignin is extracted with aqueous HCl and dioxane mixture.

Lignin can also be separated from milled wood by mixing with a nonswelling solvent such as toluene and from the suspension liquid is extracted with a dioxane–water mixture.

Lignin is a three-dimensional polymer or polymers of phenylpropane units. Whether or not lignin is bonded to carbohydrates in the wood, its properties are characterized as those of an infinite network that requires chemical degradation for solution.

The electron micrographs show lignin has an amorphous granular structure that exhibits no intimate connection with cellulose. The x-ray diffraction test ruled out the crystalline structure of lignin.

Lignin solubility suggests that there are no highly specific solvent requirements for lignin which indicates that it is an aromatic polymer with many hydroxyl groups. The solubility behavior of lignin is that which should be expected of a polar aromatic polymer with many hydroxyl groups.

Lignin fragments of lower molecular weight are more soluble in a wide range of solvents than higher molecular weight components. The swelling and solubility of lignin is greater with hydroxylated solvents, e.g., methanol, ethanol, phenol, and water than nonpolar solvents like benzene. Although native lignins behave as an insoluble, three-dimensional network, isolated lignins exhibit maximum solubility in solvents including, for example, dioxane, acetone, methyl cellosolve (ethylene glycol monomethyl ether), tetrahydrofuran (THF), DMF, and DMSO. Other polymers like natural rubber, thiokol, PVC, polystyrene, and polyisobutylene show similar behavior to lignin.

The ability of solvents to dissolve or swell a variety of isolated lignins increases as the hydrogen-bonding capacity of the solvents increase and as their solubility parameters approach a value of around $11\,(\mathrm{cal/cc})^{1/2}$. That is, lignin fractions are most soluble in solvents with solubility parameters of around 11.

The solubility of lignin decreases abruptly in alcohols with increasing hydrocarbon chain length, even when the solubility parameter is close to a value of 11 in the higher members. The high association of pure alcohols frequently results in a lower solvent power than expected.

The hydrogen-bonding capacities of various solvents are proportional to the shift in wave length of the infrared region of the spectrum. Schuerch (1952) tested several solvents and found that those having shift in wave length values of 0.14 μm or higher and solubility parameters around 11 are good lignin solvents, for example acetone, dioxane, pyridine, and glycol ethers.

The solubility of lignin is greater in the mixture than in either solvent alone. The hydrogen-bonding capacity of the mixture is greater than that of one individual solvent and often the solubility parameter of the mixture is higher than the pure solvent. The mixture of alcohol with dioxane is a more effective solvent than individual solvents (Schuerch 1950, 1965).

5. Comments

The solubility of structurally complicated materials in various solvents and liquids are not now and may never be known sufficiently well to allow attainment of that goal by tractable theoretical formulations. In this context it may be well to remember that some solubilities are cheaply determined experimentally, and can be calculated once the material is readily available. The theory of the solubility of these materials in commercial solvents and liquids is almost always too complicated and in many cases too inaccurate to be useful for direct calculation of the desired property datum at the desired condition.

There are about 1700 species of trees, including botanic and big garden collections. However, only 35 species of tree are native to the British Isles. The immense variety of trees includes species with every kind of natural distribution. Some of them occur in vast numbers across entire continents, while others are found only on one mountain or in one small valley in the entire world (Mitchell 1974).

For the study of the various properties of many wood species a large number of experimental determinations are needed which are rather time consuming and consequently expensive. The method for measuring the solubility of wood samples is outlined in Table 1.

The temperature dependence of the solubility of wood in various organic solvents has not been investigated adequately. Most of the experiments have been performed only at the boiling point temperature of the solvents in the Soxtec or Soxhlet systems (see Table 3).

The number of variables contributing to the solubility data of wood species in diverse solvents and liquids is not established yet. Some of the contributing parameters can be concluded from the discussions in Secs. 2 and 3. However, further investigations are required for better understanding of the solubility mechanism of structurally complicated materials.

For some of the wood considered, only one single measured solubility value is available. It is particularly noteworthy that only one source has provided the only reported data for solubility.

The currently available solubility data from journal publications are not sufficient for critical evaluation. In all cases, the solubility data are too few and accuracy too low. All data in Table 3 have been classified as tentative often only because comparable data have been lacking. It is concluded that there is a need for more accurate solubility data.

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