

Solvents for Cellulose

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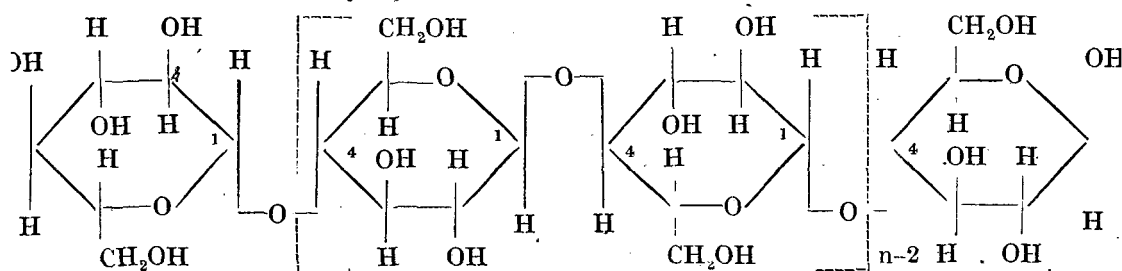
IN the chemical sense, cellulose is defined as the fibrous carbohydrate that forms part of the cell wall of plants, derived exclusively from glucose and resembling cotton, the seed hair from the genus "Gossypium", in its physical and chemical properties. Cotton cellulose differs from other celluloses in that it can be spun into yarn, a property which is also shown by certain other fibrous materials like flax, linen, ramie, jute, etc. Cotton does not consist of cellulose only, as it contains, in addition, a number of other materials related to cellulose, as also other substances like fats, waxes, colouring matter and inorganic ash. The non-cellulosic materials are removed by mechanical purification processes followed by extraction with organic solvents and aqueous alkaline solutions, bleaching with sodium hypochlorite and subsequent acidification followed by thorough washing. Purified cellulose so obtained can be fractionated into at least three components based on its solubility in 17-18% aqueous sodium hydroxide solution at 20°C. That portion of cellulose which is insoluble in the above alkali and is completely oxidised to carbon-dioxide when treated with acidic dichromate, is referred to as *alpha* cellulose and is the purest form of cellulose. That portion of cellulose, soluble in 18% aqueous sodium hydroxide solution, but which precipitates on acidification is *beta* cellulose, whereas *gamma* cellulose remains in solution even after acidification. Only *alpha* cellulose

is of scientific and industrial importance and unless otherwise stated, by cellulose one means *alpha* cellulose.

Cellulose is the most abundant of all naturally occurring organic compounds and probably makes up at least a third of all the vegetable matter in the world. It is the main constituent of the cell walls of higher plants, having received its name for this reason. It is also found in the mineral kingdom, e.g. peat and lignite, and in the animal kingdom e.g. certain marine organisms. Cellulose is also present in "*Acetobacter xylinum*."

From an industrial point of view, only cellulose from plant material is of importance. Various grasses, canes, bamboos, soft and semi-soft woods have been used as sources of cellulose and by successful chemical treatment highly purified *alpha* cellulose can be obtained, which, however, has to be further processed in order to convert it into a form that could be spun readily into yarn. Such regenerated celluloses are usually referred to by the generic expression "Rayon." The rayons are chemically identical with cellulose, but differ in certain physical properties.

Cellulose is a linear polymer built up of glucose anhydride units, linked together through the 1 and 4 carbon atoms, with *beta* glucosidal linkage as shown below :



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Though the 1:4 linkage is generally accepted, certain reactions of cellulose show the possibility of other types of linkages, e.g. 1:6 or 4:4, though unambiguous proof for their existence is lacking. Barring the two end glucose units, those in the body of the chain have three hydroxyl groups, one of which is primary and the other two are secondary. The terminal glucose anhydride residues are distinguished by the presence of a reducing hemiacetal group at one end and by the presence of an extra hydroxyl group on the fourth carbon atom, at the other.

The molecular weight of cellulose is usually given in terms of the number of glucose units or degree of polymerisation, which for *alpha* cellulose is of the order of 1,000. However, cellulose is a polymolecular material and the values obtained for the degree of polymerisation are only average ones. Recently, fractions having a degree of polymerisation as high as 15,000 have been reported.

Although chemically cellulose is a glucose polymer, in the physical sense it is a polymer of cellobiose which is *beta* anhydro diglucose, as has been shown by X-ray studies. Cellulose, because of its long range order along the chain, possesses fibre crystallinity. According to modern views, cellulose is a cryptocrystalline macromolecular substance.

The solid consists of submicroscopic crystalline regions alternating with non-crystalline ones. The degree of crystallinity varies usually from 50-70%. The geometric pattern or arrangement of the glucose units repeating itself in all the three directions is called the 'Unit Cell.' The dimensions of the unit cell are $a = 8.35\text{\AA}$, $b = 10.3\text{\AA}$, $c = 7.9\text{\AA}$ and $\angle \beta = 84^\circ$. There is, however, no general agreement as to the manner in which unit cells are distributed in space.

Cellulose has a fairly high density, the value varying with the degree of crystallinity. The density values obtained¹ by displacement techniques for raw cotton is 1.6095. The specific heat of cotton is 0.304.² Cellulose does not melt on heating as it very readily undergoes dehydration. It is a poor conductor of heat and electricity.

A solvent can be defined as a volatile fluid by means of which a solid or semisolid material may be converted without chemical change into a fluid solution. Furthermore, the removal of the solvent should result in the original substance being obtained in a chemically unaltered form.

A "molecular" (as opposed to "ionic") solution is a homogeneous system in which each solute molecule is so thoroughly dispersed in the solution that intermolecular forces are almost at a minimum. There is, however, no chemical combination between the solute and solvent molecule resulting in any permanent change. Such an ideal state is only obtained at very low concentrations, particularly in the case of high polymeric substances. Polymers in general have a tendency to occur as aggregates in solution, though at very low concentrations and in the appropriate type of solvent, true solutions can be obtained. In the above sense, there is no true solvent for cellulose. In fact, with the possible exception of methane sulphonic acid (B.P. 167° at 10mm., M.P. +20°C) cellulose is insoluble in all simple liquids. It, however, dissolves in certain solutions, particularly, aqueous solutions; but cellulose does not occur as such in solution, as it combines with some of the dissolved molecules or portions of molecules, and the complex so formed is dispersed in the rest of the medium. With the aqueous solution, removal of the volatile component does not result in the original cellulose being obtained in

unaltered form, but cellulose can be regenerated by chemical treatment.

A number of liquids, however, swell cellulose, though by themselves they are unable to dissolve it. This particular aspect is referred to later.

For the sake of convenience the solutions can be divided into two broad groups:—

(1) Aqueous solutions and

(2) Non-aqueous solutions.

Aqueous solutions, in turn, can be further subdivided into three sub-groups: (a) Acidic solutions, (b) Alkaline solutions and (c) Salt solutions.

1. (a) *Acidic solutions*: Cellulose is soluble in 40% hydrochloric acid, 72% sulphuric acid, 66% hydrobromic acid, concentrated hydroiodic acid and 75% hydrofluoric acid. Cellulose also dissolves in selenic and arsenic acids and on treatment with SO_2 gas in presence of water at $120\text{--}160^\circ\text{C}$. Cellulose can also dissolve in syrupy phosphoric acid provided it is first ground with water, when possibly a certain amount of degradation can occur. Nitric acid is a good solvent for cellulose but solution results in nitration, stable cellulose nitrates being formed. Solutions in mineral acids are generally unstable as depolymerisation occurs, the rate being dependent on temperature.

(b) *Alkaline solutions*: Aqueous sodium hydroxide solution is by far the most important solvent for cellulose. Maximum solvent power is obtained at a concentration of 2N. However, solutions are obtained at subzero temperatures and at ordinary temperatures, cellulose is insoluble in aqueous sodium hydroxide solutions. Potassium, lithium, rubidium, barium, calcium and ammonium hydroxide solutions are inferior to sodium hydroxide as solvents; but aqueous solutions of tetra-alkyl ammonium, phos-

phonium, arsenium and selenonium bases dissolve cellulose, the solvent power increasing with the molecular volume of the base. Solutions of quaternary benzyl ammonium hydroxides, like diethyl phenyl, dimethyl tolyl, etc. as also oxides of tertiary amines, like triethylamine oxide, dissolve cellulose. The solubility of cellulose in aqueous alkaline solution is enhanced when some metal hydroxides like those of zinc, copper, cobalt, beryllium⁴, etc. are dissolved in it. The requirements for good solubility are, high solubility of the hydroxide in alkali and low stability of the complex solution in contact with the —OH groups of the cellulose. The most suitable solutions are:

$\text{Zn}(\text{OH})_2$ or $\text{Be}(\text{OH})_2$ in NaOH and $\text{Cu}(\text{OH})_2$ in NH_4OH or ethylene diamine. Less active are solutions of $\text{Ni}(\text{OH})_2$ in NH_4OH and $\text{Cu}(\text{OH})_2$ or $\text{Co}(\text{OH})_2$ in NaOH. In all these cases the solubility of cellulose increases with decrease in temperature.

(c) *Salt solutions*: Cellulose has some tendency to dissolve in concentrated solutions of salts which are very soluble in water and alcohols. A hot concentrated solution of $\text{Ca}(\text{CNS})_2$ has been described as a good solvent for cellulose. A number of salt solutions dissolve cellulose which is more or less degraded. The degree of solvent power follows the lyotropic series increasing in the order—

Cl, NO_3 , Br, I, SCN and

Ca, Mg, and K, NH_4 , Na, Li.

The solubility in salt solutions can be enhanced if the solutions are not neutral. Thus basic beryllium perchlorate can dissolve cellulose even in the cold and similarly acidic ZnCl_2 or $\text{Ca}(\text{CNS})_2$ are better solvents.

2. Among the non-aqueous solutions, only solutions of certain organic

compounds in liquid N_2O_4 are of importance.⁵ The requirements for good solubility are, that the organic compound must contain an electro-negative group in the molecule and exhibit very slow reactivity or none with N_2O_4 , as well as a range of miscibility or solubility with the latter. Among these the alkyl and aryl nitrocompounds are by far the most important, though acetates, benzoates, nitriles, as also benzo phenones are equally effective. However, as N_2O_4 has a very low B.P., solutions are likely to be obtained only at low temperatures. Furthermore, as N_2O_4 reacts with the primary hydroxyl group of the glucose unit, the solution may not be molecular except in the earlier stages.

Cellulose solutions, when freshly made, show all the characteristics of solutions of high polymers. They show high viscosity even in dilute solutions, low freezing point depression and boiling point elevation, as also low osmotic pressure. Because of the large molecular magnitude, it shows certain colloidal behaviour, as for example, slow rate of diffusion and tendency to flocculate. Solution of cellulose is accompanied by a positive heat effect in contrast to the behaviour of other macromolecular compounds. Cellulose solutions, particularly those in strong acids, degrade very rapidly at ordinary temperature but at low temperatures fairly stable solutions may be obtained. Degradation causes break in chain and longer the chains greater are the chances of breakage.

Cellulose does not occur in its original form in solution, but as a complex with some of the molecules present in solution. With acids, cellulose might give an oxonium salt, the $-OH$ group accepting a proton from the acid being converted into the ion $-OH^+$. Similarly, an alcoholate is formed in alkalies and a co-ordinate complex in salt solutions. The type of complex formed varies in its stability and in certain cases (e.g.

solution in triethylamine oxide) the original cellulose can be isolated by simple dilution with water. Even the action of water can be looked upon as a chemical action, the bond being susceptible to hydrolysis by water alone. Solutions in aqueous alkali are stable provided air or O_2 is excluded and in fact measurement of viscosity or osmotic pressure of cuprammonium or cuprethylenediamine solutions are used to determine the degree of polymerisation of cellulose. However, the cellulose actually combines with the base and even in molecular weight determinations a correction has to be applied. Solubility in tetraalkyl ammonium and similar bases is to be attributed to the formation of specific co-ordinate structures with basic properties.

It is possible that similar co-ordinate complexes are formed in salt solutions also, though no specific proof is available. In all the cases, cellulose cannot be isolated from the solution by mere dilution; acidification is essential.

As mentioned before, a number of liquids have the ability to swell cellulose, although they are unable to dissolve it. A solid is said to swell when it takes up a fluid, while at the same time it does not lose its apparent microscopic homogeneity, its dimensions are enlarged and its cohesion diminished, resulting in a decrease of the elastic modulus. The fluid occurs as a condensed phase within the solid and is actually in combination with it and as such it cannot be removed by simple mechanical methods. In other words, the fluid is not simply adsorbed but absorbed within the whole body of the solid.

Swelling of cellulose can either be intercrystalline or intracrystalline; furthermore the extent of swelling may be limited or unlimited. In limited swelling the cellulose swells only up to a certain extent and does not terminate, in com-

plete dissolution. Unlimited inter- and intra-crystalline swelling is necessary in order to obtain complete solution.

A number of liquids, as also solutions, cause swelling of cellulose, of which water, liquid ammonia, lower alcohols and ethylene glycol are the most important. Aqueous solutions of urea, thiourea, chloral hydrate, resorcinol, etc. are actually superior to water, as swelling agents.

The swelling of cellulose in any liquid or solution is dependent on its dielectric constant, ionic density and size and shape of the molecule. Some of these liquids or solutions cause only inter-crystalline swelling, alkalies being the typical representatives of this group. Acidic substances, on the other hand, cause intra-crystalline swelling, though the extent with the usual liquids is comparatively limited. The solvents proper, as is to be expected, cause both inter- and intra-crystalline swelling.

The solution of cellulose in any particular liquid or solution is invariably preceded by swelling. This is particularly the case in acid solutions. In the alkaline solutions, the total swelling that is observed is not a true measure of the extent of swelling, as a certain amount of shrinkage is supposed to occur. While the concepts based on the effect of hydro-static pressure and the like have been questioned, it is possible that the alkali is causing dissolution of the molecules at the surface, with simultaneous swelling of inter-crystalline regions, but with little or no intra-crystalline swelling.

The reason for the restricted solubility of cellulose and even the limited amount of swelling in the majority of liquids can be attributed to its chemical and physical structure. Each cellulose molecule has three hydroxyl groups per glucose unit and the number of such

glucose units may be anywhere from 1,000 upwards. Thus the number of hydroxyl groups per cellulose molecule is very large. Also, since the hydroxyl group possesses very high molar cohesion, the total cohesive force is very large, and as the area over which this is effective is small, the cohesive energy density of the cellulose molecules is very high. Because of the rigidity introduced in the molecule by the 6-membered ring system of the glucose unit and lack of freedom of movement about the oxygen bridge, coupled with an absence of long side chains, chain segment movement is almost non-existent. Hence, cellulose is rather a difficult substance to dissolve. In order to get cellulose in solution, the forces between the polymer molecules must be minimised or overcome. This is done by solvation and swelling.

Solvation can be looked upon as binding of the solvent molecules to the chain molecules. Thus, solvents containing groups which are capable of being bound to the hydroxyl of the cellulose are good solvating agents. Solvation by itself does not promote solubility unless it results in swelling. While the swelling of the intercrystalline regions is comparatively easy because of ready accessibility of the cohesive groups and very low energy barrier that is to be overcome, the swelling of the intracrystalline region necessitates a larger expenditure of energy. Furthermore, the large changes in free energy that are involved may actually promote the formation of a new crystalline phase in addition to causing a breakdown of the original crystal lattice. It is therefore, not surprising that only a very limited number of molecules are able to cause unlimited intra-crystalline swelling. Acid solutions of strength other than that mentioned elsewhere do cause a change in the degree of crystallinity, a constant value being obtained after treatment, irrespectively of the original degree of crystallinity. The extent of

intracrystalline swelling will also depend on the distribution of the crystal regions within the macrostructure and generalisations are not possible.

Thus, cellulose or its co-ordinate complex occurs in an ionic form in solution, and as such no true solvent, where the cellulose can be present in a molecular form, is known. However, it should be possible to synthesise a compound which will have all the characteristics of high dielectric constant, coupled with ability to act as either a proton donor or an electron acceptor. The solutions of specific organic materials in liquid N_2O_4 are an indication as to the lines along which work will have to be carried out, if single species of molecules, preferably liquid at ordinary temperatures, are to be synthesised.

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