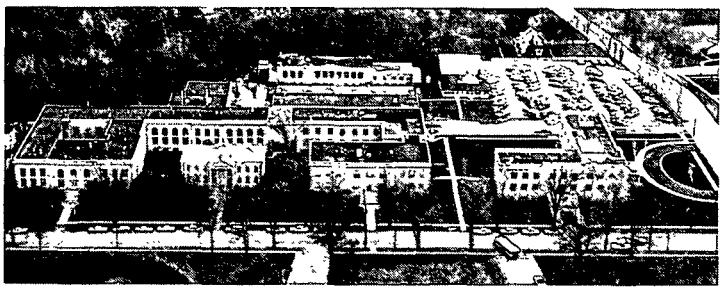

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INTRA- AND INTERMOLECULAR HYDROGEN BONDS IN NATIVE, MERCERIZED AND REGENERATED CELLULOSES: THEIR REFLECTION IN PATTERNS OF SOLUBILITY AND REACTIVITY

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Intra- and Intermolecular Hydrogen Bonds in Native, Mercerized and Regenerated Celluloses: Their Reflection in Patterns of Solubility and Reactivity

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An unusual pattern of dissolution of cellulose and related polysaccharides in the SO_2-amine-DMSO system has been observed and interpreted in terms of distinctive hydrogen bonding patterns. In particular, it was found that only native and mercerized cellulose dissolve in this system, while regenerated celluloses, glucomannan, xylan, starch, pectin and curdlan are insoluble. The pattern for the celluloses has been correlated with relative reactivities of hydroxyl groups in etherification reactions in different environments, and with results of solid state ^{13}C NMR studies on the celluloses and related oligosaccharides and polysaccharides. They suggest that the solvent system acts at particular sites involving cooperative hydrogen bonding, incorporating, among others, the primary hydroxyl group at C6 and the linkage oxygen.

Our proposal has the key implication that regenerated and mercerized celluloses have different patterns of intermolecular hydrogen bonding, even though they may have similar heavy atom lattices. This is analogous to what has been proposed as the key difference between the I_α and I_β forms of native cellulose. Taken together these findings suggest that the organization and packing of the heavy atom lattices in celluloses are dominated by the shapes of the molecules in their different conformations, and that more than one stable pattern of intermolecular hydrogen bonding is consistent with each heavy atom lattice.

The supermolecular structures of cellulose have been investigated extensively by many techniques including x-ray and electron diffractometry, electron microscopy, IR and Raman spectroscopy, broad-line proton NMR and solid-state ^{13}C-NMR. Nevertheless, many questions remain concerning the solid-state structures.

During our studies on cellulose chemistry (1-5), we have encountered an unusual pattern of solubilities of various celluloses and related polysaccharides in one of the nonaqueous cellulose solvent systems we investigated, the SO_2-diethylamine(DEA)-dimethylsulfoxide(DMSO) system. In this paper, we propose an interpretation of this pattern in terms of intra- and intermolecular hydrogen bonds in native, mercerized and regenerated celluloses. We also consider parallels with the relative reactivities of hydroxyl groups in glucose residues of cellulose toward etherification, under basic conditions, and the data from solid-state ^{13}C-NMR reported by Atalla and others (6-9).

Experimental

Sample Preparations. The native celluloses used were Avicel, cotton linters and ramie. Degrees of polymerization of Avicel and the cotton linters determined by the copperethylenediamine viscosity method (10) were 250 and 1360, respectively. Mercerized samples were prepared from these celluloses by stirring in 24% NaOH solution containing 1% NaBH under a nitrogen atmosphere for 20 hrs at room temperature. The samples were washed on a 1G2 glass filter with large amounts of water, dilute acetic acid, large amounts of water again and, finally, acetone. They were dried at 40°C in vacuo for 1 day. Regenerated samples were prepared from native celluloses by dissolving in cadoxene (11), and regenerating by dropwise addition to dilute acetic acid. The regenerated cellulose was filtered and washed with large amounts of water. Half of each sample was washed with acetone and dried at 40°C in vacuo for 1 day, and the other half was subjected to lyophilization followed by drying at 40°C in vacuo for 1 day.

Amylose and starch, both derived from potato, were commercial samples. Glucomannan and xylan were isolated from spruce and beech holocelluloses, respectively, and purified by the usual method (12). Pectin was isolated and purified from the midrib of Nicotiana tabacum and kindly provided by Dr. Shigeru Eda at The Central Research Institute, Japan Tobacco Inc. (5).

The solubility of the polysaccharides was tested by dispersing 1 g of a dried sample in 42 ml DMSO, and then adding the SO_2/DMSO solution containing 1.19 g of SO_2 (4.09 ml of 0.291 g SO_2/ml DMSO solution) and 1.92 mo DEA, in this order at room temperature. Successful dissolution was judged by visual examination after stirring for 1 day.

Results and Discussion

1. Solubilities of celluloses and other polysaccharides in the SO_2-DEA-DMSO system

In our previous work on the derivatizations of cellulose (1-5), we have found the SO_2-DEA-DMSO system to be the most effective nonaqueous cellulose solvent medium for the preparation of highly substituted cellulose ethers. The solubilities of various cellulosic samples and other polysaccharides in this nonaqueous solvent system were tested in the course of the investigations. As shown in

Table I, native celluloses such as ramie, cotton linters and Avicel, both before and after mercerization dissolved completely in this solvent system. More recently we have established that highly crystalline algal celluloses are also readily dissolved in this system.

Table I. Solubilities of Various Polysaccharides in SO_2-diethylamine-DMSO System

Soluble	Native celluloses (ramie, linter, Avicel) Mercerized celluloses (ramie, linter, Avicel)
Insoluble	Amylose, starch, glucomannan, xylan, pectin Regenerated cellulose (ramie, linter, Avicel)

In sharp contrast, regenerated cellulose samples prepared from ramie, cotton linters and Avicel do not dissolve, even after decrystallization by ball-milling. Furthermore, amylose, starch, glucomannan, xylan and pectin were also found to be insoluble in this system. Our finding concerning regenerated samples is consistent with the report by Yamazaki and Nakao (13) that commercially available rayons, even with DPv as low as 300, are insoluble in all SO_2-amine-organic solvent systems. The patterns of solubility, or lack thereof, are curious because regenerated celluloses generally have lower crystallinities than native ones. Moreover, the other polysaccharides so far examined have lower molecular weights and crystallinities than native celluloses. In addition, amylose and starch are soluble in DMSO alone above 60°C. All the cellulose samples and the polysaccharides used in this work are soluble in other nonaqueous cellulose solvent systems such as paraformaldehyde-DMSO (14), LiCl - dimethylacetamide (15), N-methylmorpholine N-oxide (16) (containing small amounts of water) and others. Thus, the insolubility of regenerated celluloses was observed only for the SO_2-amine systems. We believe that the differences in solubility reported in Table I may reflect different patterns of intra- and intermolecular hydrogen bonding in different celluloses.

In the previous work in which ^1H- and ^{13}C-NMR were used (17), the dissolution of cellulose in the SO_2-DEA-DMSO system has been explained in terms of complex formation between the -OH of cellulose, and SO_2 and DEA, as shown in Figure 1. The pattern of solubilities noted earlier suggests that the complex formation reaction in Figure 1 is specific to particular intra- and/or intermolecular hydrogen bonding patterns peculiar to native and mercerized celluloses.

The dissolution characteristics of native, mercerized and regenerated celluloses and their interpretation in terms of hydrogen bonding differences point to some interesting relationships. Native and mercerized celluloses would seem to have some common hydrogen bonding patterns, although they have different x-ray diffraction patterns. On the other hand, mercerized and regenerated celluloses would differ from each other with respect to intermolecular hydrogen bonds, although they have the same x-ray pattern.

Recently, VanderHart and Atalla (18) proposed,on the basis of CP-MAS ^{13}C NMR of different cellulose samples, that all native celluloses are composites of two crystalline modifications, cell I_α and I_β, even though they have similar x-ray patterns. These have been interpreted in terms of similar heavy atom lattices with different hydrogen bonding patterns (19,20). Thus, it may well be that mercerized and regenerated celluloses differ in the same way and can have different intermolecular hydrogen bonding patterns, which result in differences in their solubility in the SO_2-DEA-DMSO system.

2. Relative reactivities of hydroxyl groups in glucose residues of cellulose toward etherifications under basic conditions

We have previously reported studies on the distribution of substituents in partially etherified celluloses which were prepared from heterogeneous alkali cellulose and from homogeneous nonaqueous cellulose solutions (21). In the latter case, partially substituted cellulose ethers such as methyl- and carboxymethyl-celluloses were prepared from SO_2-DEA-DMSO solutions of cellulose by additions of powdered NaOH as a base.

When the nonaqueous cellulose solvent was used as a medium, the order of reactivities was 6-OH>2-OH~3-OH. This order is similar to observations in the case of simple alcohols. Thus, although the primary hydroxyl group 6-OH has the highest reactivity, and the secondary hydroxyl groups 2-OH and 3-OH have almost equal reactivities, the difference of reactivities between 6-OH, 2-OH and 3-OH is small. On the other hand, when heterogeneous alkali cellulose systems were used, where cellulose was swollen in aqueous alkali rather than being in solution, the order of reactivity was 2-OH>6-OH>>3-OH at all concentrations of aqueous alkali (22). This order is not consistent with the pattern for lower molecular weight compounds and suggests consideration of effects of intra- and intermolecular hydrogen bonds which may remain even in swollen alkali cellulose. The secondary hydroxyl group 2-OH has a higher reactivity than the primary alcohol 6-OH, and there is a remarkable difference in reactivities between the secondary alcohols 2-OH and 3-OH. These results suggest that some of the intramolecular hydrogen bonds between the 3-OH groups and O-5 in the adjacent anhydroglucose residues, known to occur in native celluloses, are retained even in swollen alkali cellulose, and thus have an effect on the etherification process.

The resistance to disruption by alkali also suggests some strong intermolecular hydrogen bonds in cellulose. Such strong hydrogen bonds may well be the key to retention of the fiber form of alkali cellulose at all concentrations of alkali. In the case of most polymers, swelling and dissolution in solvents proceed in sequence. That is, first the accessible parts are swollen by a solvent and this is followed by dissolution. However, in the case of cellulose in aqueous alkali, although it is swollen and undergoes a lattice transformation, it does not dissolve. If the hydroxyl groups are solvated with aqueous alkali and if all intra- and intermolecular hydrogen bonds are cleaved, cellulose fibers cannot be expected to keep their form nor to form a new lattice. This suggests that

some of the strong intermolecular hydrogen bonds in native cellulose may survive in swollen alkali celluloses and contribute to the definition of the new lattice. Such a proposal seems a plausible alternative to that of Na^+ stabilization of the lattice.

It has been proposed that in alkali cellulose, alkali (NaOH) and water bridge the cellulose molecules (23). However, it does not seem likely that all direct intermolecular hydrogen bonds in alkali cellulose are disrupted, inasmuch as the fibrous morphology is retained. Additionally, there have not been any reports of any precipitates of complexes between oligomers and alkali in aqueous solutions.

There has been another proposal that plane-structures consisting of cellulose molecules in the 101 plane of native cellulose are held together by hydrophobic interactions even in the presence of alkali, and that hydrophilic surfaces of the 101 plane-structures are solvated with alkali and water (24). However, if such planar structures were solvated with aqueous alkali, they would be expected to result in the formation of a dispersion of micelles. It seems to us more likely that some strong or sterically protected intermolecular hydrogen bonds of native cellulose survive even in alkali cellulose. On the other hand, since some hydrogen bonds are cleaved by NaOH and water which penetrate into the crystalline lattice of cellulose, new lattice planes can be formed as, for example, in Na-Cellulose I or other soda celluloses.

In assessing the stability of intermolecular hydrogen bonds, the pattern of chemical reactivity of the hydroxyl groups may be an indicator. On the basis of the results of relative reactivities of the hydroxyl groups in the anhydroglucose residues, the more stable intermolecular hydrogen bonds of cellulose appear likely to involve 6-OH, because it often shows lower reactivity for etherifications than the 2-OH.

3. Solid-state 13C-NMR data of various cellulose samples

^{13}C-NMR spectral shifts for cellulose and some oligomers are summarized in Figure 2 (6-9). Horii et al. (9) discussed the chemical shifts of C-6 carbons, and proposed that the difference between Cellulose I and Cellulose II is caused by conformational differences at the 6-OH groups. The shifts in the crystalline parts of Cellulose I were assigned to t-g conformations (ca. 66 ppm for C-6), and those for Cellulose II and the amorphous parts of all celluloses to g-t conformations (ca. 63 ppm for C-6).

In contrast, chemical shifts of the C-4 carbons change largely depending on whether cellulose is in a solid state or in solution (Figure 2). Horii et al. (25) suggested that this change in the chemical shift of C-4 is also caused by conformational difference. However, such a high downfield shift of C-4 carbons (Δ = ca. 10 ppm) seems unlikely to arise from a conformational difference alone. Changes in chemical shifts of carbons in low molecular sugars, which have been reported by Horii et al. (9), were explained mainly in terms of changes in shielding due to different hydrogen bonding patterns associated with different conformations.

The solid-state ^{13}C-NMR spectra of curdlan, amylose and chitin have also been reported (26), and generally C-1 and C-4, or C-3 in

the case of curdlan, have high chemical shifts in their solid states in comparison with shifts in solution. Table II shows the difference (Δ) between the chemical shifts in the solid state and in solution for the above glucans as well as cellulose. The table shows that Δ for C-1 carbons ranges from 1.0 to 3.0 ppm. In the case of amylose and chitin Δ's for C-4, and in the case of curdlan Δ for C-3, are only slightly higher (4.1-4.5 ppm). On the other hand, cellulose has a much larger Δ of 10 ppm for C-4. This exceptionally high chemical shift for C-4 suggests a special difference for solid-state structures of celluloses.

Table II. Difference (Δ, ppm) of ^{13}C-Chemical Shifts Between Solid and Solution States

Sample	Linkages	Δ, ppm C-1	Δ, ppm C-3	Δ, ppm C-4
Curdlan	(1-3)-β-D-glucan	1.0	4.2	
Amylose	(1-4)-α-D-glucan	2.3		4.5
Chitin	(1-4)-β-D-2-acetamido-2-deoxy-glucan	2.3		4.1
Cellulose	(1-4)-β-D-glucan	3.0		10.0

We propose here a possible explanation for the high value of the chemical shifts of C-4 in crystalline cellulose, namely, as represented in Figure 3, an exceptionally strong intermolecular hydrogen bond between a 6-OH and a glycosidic linkage oxygen atom. We speculate that it is the 6-OH of an adjacent chain because of the anomalously low reactivity of the primary hydroxyls in soda celluloses. Stabilization of such an intermolecular hydrogen bond can be facilitated by a transfer of electron density to the glycosidic oxygen atom from the C-4 carbon. This, in turn, can reduce the shielding at C-4 and result in the downfield shift of its resonance. Electron density at C-1 is clearly too low for it to make a significant contribution because of its anomeric character; this is reflected in its downfield shift beyond 100 ppm. Strong intermolecular hydrogen bonds stabilized by the shift of electron density could be resistant to cleavage even in concentrated aqueous alkali, and thus stabilize the morphology of the fiber.

Discussion

The results discussed in the previous sections suggest one property common to native and mercerized celluloses which is not shared by regenerated celluloses. That is their solubility in the SO_2-amine-DMSO system. On the other hand, mercerized cellulose and regenerated cellulose possess very similar x-ray diffraction patterns, though their response to the solvent system is not the same. These patterns suggest differences between mercerized and regenerated celluloses analogous to the differences between I_α and I_β, among the components of native celluloses. Thus it is proposed that, although

mercerized and regenerated celluloses possess the same or very similar heavy atom lattices, the patterns of hydrogen bonding developed during regeneration are unlike those which result from mercerization. Furthermore, it appears that the system of hydrogen bonds that is the specific site of attack of the SO_2-amine-DMSO system is not formed during the regeneration of cellulose from solution.

Whether the hydrogen bond of the primary hydroxyl to the glycosidic linkage oxygen is a part of this system remains an open question, since the unusually high downfield shift of the ^{13}C-NMR resonance of C-4 also occurs in regenerated cellulose. It seems more likely that this hydrogen bond is part of a system of hydrogen bonds that act in concert and result in a cooperative stabilization of the system for native and mercerized celluloses. Thus, while the C-6 hydroxyl hydrogen bond to the glycosidic linkage may be formed in regeneration, the other components of the cooperative hydrogen bond system do not occur. If the action of the SO_2-amine-DMSO solvent is particularly attuned to the cooperative hydrogen bonding effect, its inability to solubilize regenerated cellulose, or any of the other polysaccharides can be accounted for.

The proposal we make here is a speculative one. We believe it valuable to present it, however, particularly in view of the differences in hydrogen bonding patterns of the I_α and I_β celluloses alluded to above. The implications of our proposal are quite important in the context of structural studies on cellulose in general, for it follows from the proposal that the packing of the heavy atom lattice is determined primarily by the shape of the molecules in their different conformations and that more than one stable pattern of hydrogen bonding is possible for each of the heavy atom lattices.

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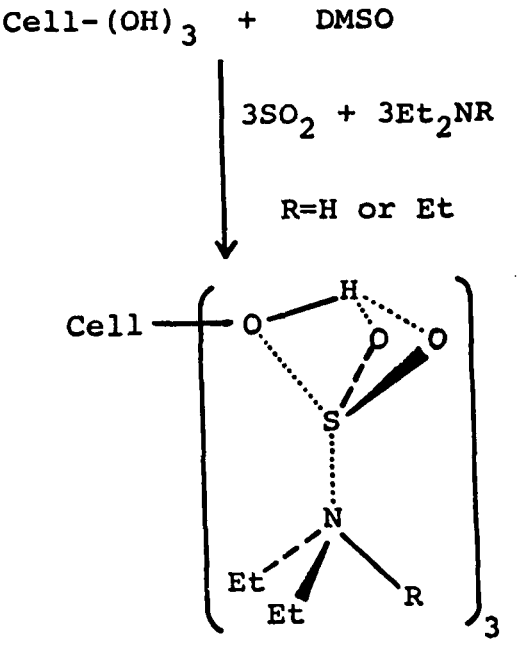

Figure 1. Dissolution mechanism of cellulose in SO_2-amine-DMSO systems.

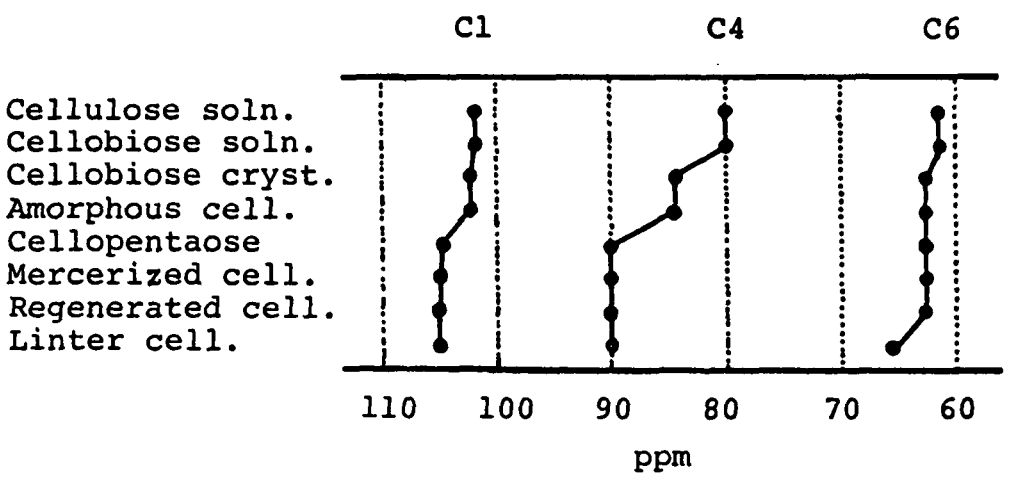

Figure 2. ^{13}C-chemical shifts of carbon in various cellulose samples.

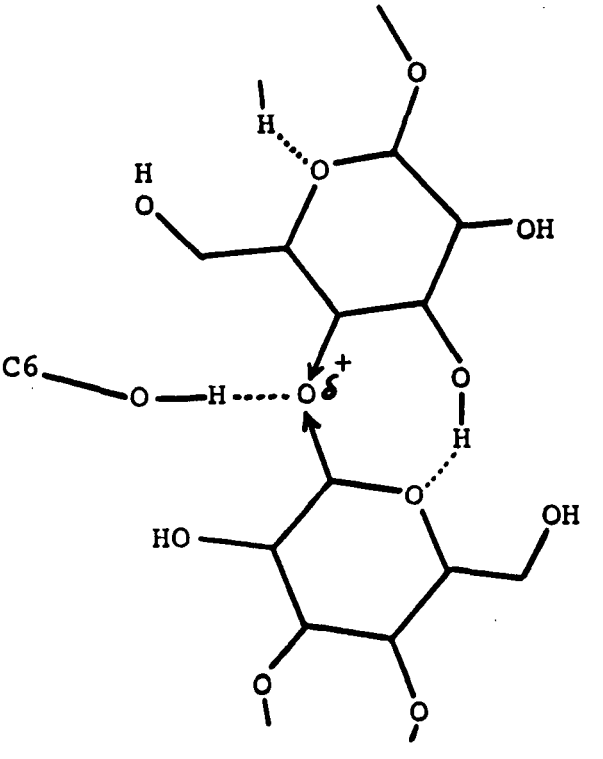

Figure 3. Possible intermolecular hydrogen bond in cellulose.