

Solid State ^{13}C NMR Spectra Analysis of Alkalicellulose

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ABSTRACT: Changes in CP/MAS ^{13}C NMR spectra, T_{1c} and WAXS of alkalicellulose with alkali concentration were investigated to clarify the presence of a selective coordination of Na^+ and intra- and intermolecular hydrogen bonds. $\text{O}_3\text{-H}\cdots\text{O}_5'$ intramolecular hydrogen bonds and $\text{O}_2\text{-H}\cdots\text{O}_6'$ intermolecular hydrogen bonds exist in the original sample (Cell I). By selective coordination of Na^+ to the hydroxyl group at C_2 which is the most probable, the $\text{O}_2\text{-H}\cdots\text{O}_6'$ intermolecular hydrogen bond is broken. At coordination above 25.0 wt% NaOHaq, the $\text{O}_3\text{-H}\cdots\text{O}_5'$ intramolecular hydrogen bond is broken by selective coordination of Na^+ to O_3 at C_3 . Each carbon's T_{1c} of Na-Cell treated with a concentration above 15.0 wt% NaOHaq becomes shorter than that of Cell I. This phenomenon thus appears due to the destruction of intra- and intermolecular hydrogen bonds.

KEY WORDS Alkalicellulose / CP/MAS ^{13}C NMR / Cellulose I / WAXS / Hydrogen Bond / Relaxation Time /

Since alkalicellulose is chemically highly reactive, cellulose ethers are at present commercially synthesized on a large scale *via* alkalicellulose as an intermediate compound from cellulose. It is widely recognized that the reactivity of alkalicellulose against other chemical reagents and distribution of substituent groups of cellulose derivatives formed depend remarkably on the solid state structure of alkalicellulose. However, we have never obtained directly detailed information on the higher order structure of cellulose solid.

Recently,¹⁻⁷ it has been demonstrated that high-resolution solid-state ^{13}C NMR, using the cross polarization/magic angle sample spinning (CP/MAS) technique, is a very good method for studying the backbone conformations of cellulose. CP/MAS ^{13}C NMR spectra are sensitive to changes of chain conformation and packing density as well as a specific changes in the chemical environment of the different OH-groups of the anhydroglucose units.

In this paper, we investigate changes in CP/MAS ^{13}C NMR spectra, spin-lattice relaxation times (T_{1c}) and wide angle X-ray scattering (WAXS) with alkali concentration in order to clarify the presence of a selective coordination of Na^+ and the intra- and intermolecular hydrogen bonds in alkalicellulose.

EXPERIMENTAL

The starting material of cellulose I (Cell I) was ramie, of which crystallinity measured by X-ray diffraction methods was about 85%. Sodium cellulose (Na-Cell) was prepared from ramie by treatment with 10.0, 12.5, 15.0, 17.5, 20.0, 22.5, 25.0, 30.0, 35.0, 40.0, and 45.0 wt% aqueous sodium hydroxide solution at 20°C for 1 h under a condition that the fibers were allowed to shrink freely. After hand-pressed to exclude excessive alkali from the sample, the Na-Cell was dried in a desiccator.

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^{13}C NMR spectra were recorded by a JEOL JNM-GX270 spectrometer under the following conditions: Static magnetic field, 6.34 T; resonance frequency, 67.8 MHz; radiofrequency field strength used for dipolar decoupling (DD), 45.5 kHz ($5.5\ \mu\text{s}$); cross-polarization contact time, 2 ms; repetition time, 5 s; rotational velocity of MAS, 3 kHz; measuring temperature, room temperature. Chemical shifts δ relative to tetramethylsilane were determined using a narrow crystalline resonance line at 29.5 ppm for solid adamantane. The specimens wound into ball, were packed closely in a rotor.

Spin-lattice relaxation times, T_{1c} , were measured for each carbon under the CP condition by application of the pulse sequence developed by Torchia.⁸

WAXS patterns of samples were obtained by the technique described in (1).

RESULTS AND DISCUSSION

Figure 1 shows CP/MAS ^{13}C NMR spectra of ramie in Cell I and its alkalicelluloses A (12.5 wt% NaOHaq.), B (15.0 wt%) and C (25.0 wt%). Peak assignment was carried out using the results of Horii *et al.*²⁻⁵

Figure 2 shows a comparison of ^{13}C chemical shifts of alkali-treated samples after steeping with aqueous NaOH solutions of various concentrations. These ^{13}C chemical shifts are divided into A (—12.5 wt% NaOHaq.), B (15.0—22.5 wt%), and C (25.0—45.0 wt%) groups depending on the alkali concentration. Namely, Figure 2 gives the following results:

(1) For (A) group, all carbon peaks are observed at almost the same position as those of Cell I.

(2) For (B) group, the C_1 and $\text{C}_{2,3,5}$ carbon peaks shift towards a slightly lower magnetic field, but the C_4 and C_6 carbon peaks towards a higher magnetic field, compared with those in Cell I.

(3) For (C) group, the C_4 carbon peak is superposed with the $\text{C}_{2,3,5}$ carbon peaks, so

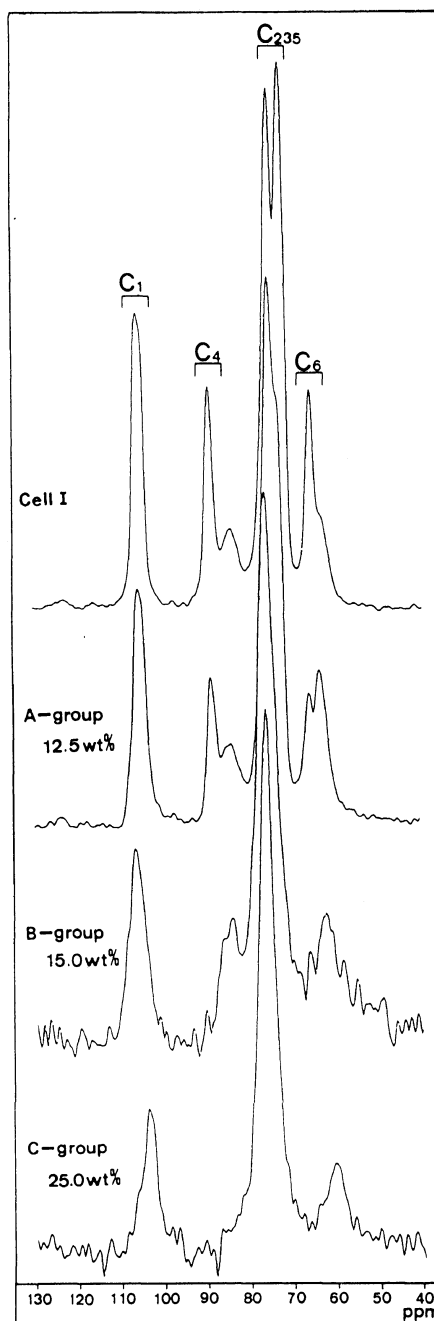


Figure 1. CP/MAS ^{13}C NMR spectra of ramie in Cell I and of its alkali celluloses A (12.5 wt% NaOHaq.), B (15.0 wt%), C (25.0 wt%).

that it cannot be observed. The C_1 and C_6 carbon peaks and $\text{C}_{2,3,5}$ carbon peaks shift towards a higher and lower magnetic field,

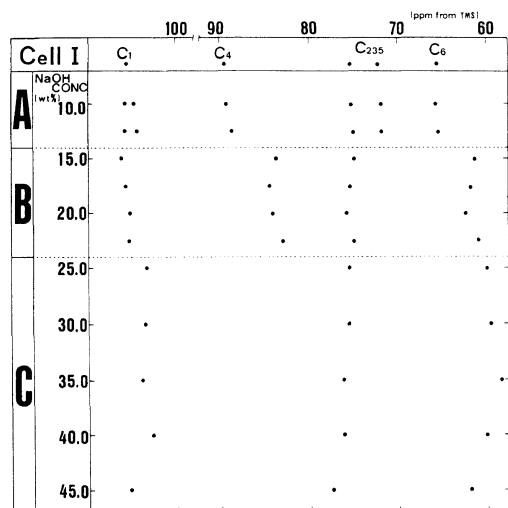


Figure 2. ^{13}C chemical shifts of alkalicelluloses after treatment with aqueous NaOH of various concentration.

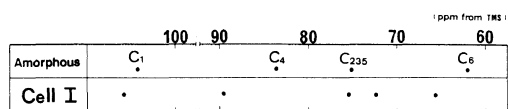


Figure 3. ^{13}C chemical shifts of amorphous cellulose and ramie (Cell I).

respectively, as compared with those in (B) group.

An attempt was made to clarify the existence of intra- and intermolecular hydrogen bonds and selective coordination of Na^+ in Na-Cell by using these chemical shifts.

Figure 3 shows the ^{13}C chemical shifts of the original sample (Cell I) and amorphous cellulose made by crushing the original sample in an automatic mortar for 210 h. Kamide *et al.*¹⁰ concluded that intra- and intermolecular hydrogen bonds in the amorphous cellulose may not conspicuously have influence on the chemical shift of the ^{13}C NMR spectrum. It is adequate as a first approximation to consider the electron charge density on given carbon atoms in view of the possible presence of hydrogen bonds in order to clarify differences of ^{13}C chemical shifts between both samples. Therefore, we assumed schematic hydrogen bonds which are an intramolecular hydrogen

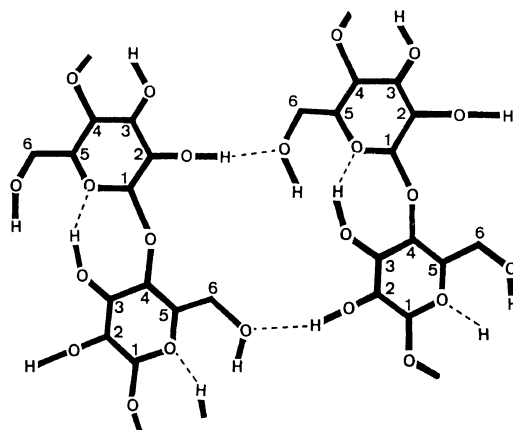


Figure 4. Possible model of intra- and intermolecular hydrogen bonds in Cell I.

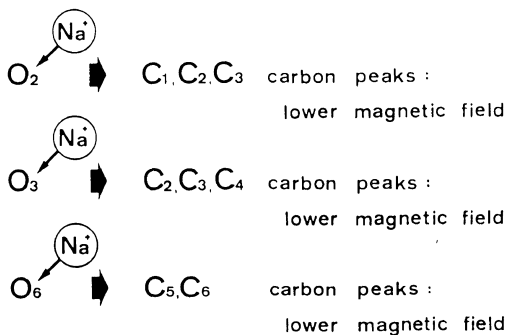


Figure 5. Possible chemical shift in the ^{13}C NMR spectrum of alkalicellulose with selective coordination of sodium ion.

bond $\text{O}_3\text{-H}\cdots\text{O}_5'$ and an intermolecular hydrogen bond $\text{O}_2\text{-H}\cdots\text{O}_6'$, as shown in Figure 4, referring to the results of IR spectroscopy and solid-state ^{13}C NMR spectra reported by Hayashi *et al.*⁹ and Kamide *et al.*¹⁰, respectively.

To explain the shifts of these peaks for (B) and (C) groups in Figure 2, the specific change in the chemical environment of an electron from the carbon adjacent to the hydroxyl group, may be considered. This change is induced by a selective coordination of Na^+ to the hydroxyl groups at C_2 , C_3 , and C_6 . Figure 5 shows possible chemical shifts of Na-Cell when Na^+ coordinates selectively to hydroxyl groups at C_2 , C_3 , and C_6 .

(B) group: When Na^+ coordinates to the O_6 at the C_6 , the C_6 and C_5 peaks must shift towards a lower magnetic field, but this selective coordination of Na^+ is not considered because the C_6 carbon NMR peak clearly shifts towards a higher magnetic field, as shown in Figure 2. The degree of selective coordination of Na^+ is expected to be greater for the C_2 carbon than for the C_3 carbon, because the hydroxyl oxygen at the C_3 position has the $\text{O}_3\text{-H}\cdots\text{O}_5'$ intramolecular hydrogen bond mentioned above.

When Na^+ coordinates to the O_2 at C_2 position, the C_1 , C_2 , and C_3 carbon peaks must shift towards a lower magnetic field, as shown in Figure 5. The C_4 carbon peak shifts towards a higher magnetic field. The cause of the shifts of C_4 carbon peak is not clear, but as the C_4 carbon is located at the γ position from the C_2 carbon, it may be considered that the peak shifts towards a higher magnetic field due to the γ effect. Furthermore, the $\text{O}_2\text{-H}\cdots\text{O}_6'$ intermolecular hydrogen bond is broken, and then the C_6 carbon peak shifts towards a higher magnetic field which is slightly higher than C_6 peak of amorphous. This probably suggests existence of one more reaction relevant to the shift. It may be a change of a conformation, because it has been reported by Horii *et al.*¹² that changes of the conformation of the CH_2OH groups correspond to that of the chemical shift of C_6 carbon. This assumption of the selective coordination of Na^+ to O_2 at C_2 agrees with experimental results of (B) group. This suggests that the distance between molecular chains is widened easily by the destruction of intermolecular hydrogen bonds.

Figure 6 gives a comparison of the X-ray diffractograms of Na-Cell. These diffractograms are divided into (A), (B), and (C) groups in the same way as in NMR spectra. The results obtained from the (B) group suggest the change of the chain packing from the Cell I type to the typical Na-Cell III type, whose lattice constant is larger than that of Cell I type.¹¹ This agrees with the discussion on the ^{13}C

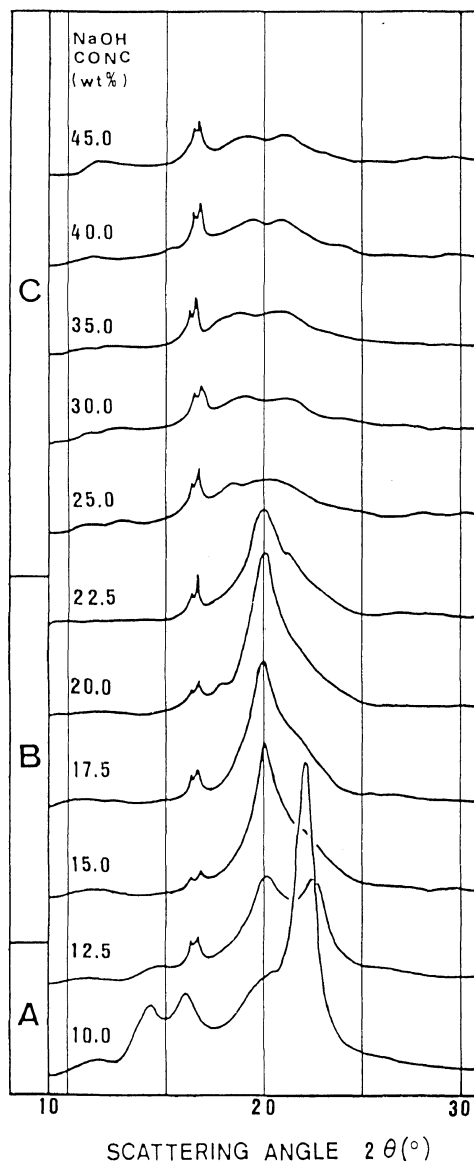


Figure 6. Equatorial X-ray diffractograms of alkalicelluloses after treatment with aqueous NaOH of various concentration.

NMR spectra for (B) group.

(C) group: A destruction of $\text{O}_3\text{-H}\cdots\text{O}_5'$ intramolecular hydrogen bonds is considered to start at 25.0 wt% NaOH aq, due to selective coordination of Na^+ to the O_3 at C_3 , because the C_1 and C_4 carbon peaks shift towards a higher magnetic field and the C_3 carbon peak

Table I. T_{1c} of each carbon in cellulose and alkalicelluloses

Group	Sample name	NaOH conc	C_1		C_4	$C_{2,3,5}$		C_6
		wt%	s		s	s		s
—	Cell I	—	89	73	97	50	81	85
A	Na-Cell	10.0	100	98	198	75	145	130
A	Na-Cell	12.5	112	107	182	61	144	101
B	Na-Cell	15.0	60		51	52		20
B	Na-Cell	17.5	51		59	28		17
B	Na-Cell	20.0	50		40	33		10
B	Na-Cell	22.5	47		25	21		11
C	Na-Cell	25.0	43		—	30		9.5
C	Na-Cell	30.0	32		—	24		8.7
C	Na-Cell	35.0	26		—	14		2.2

towards a lower magnetic field. At above 35.0 wt% NaOHaq, the effect of the selective coordination of Na^+ to the O_6 at C_6 is considered, because the C_6 carbon peaks start to shift towards a lower magnetic field. As shown in Figure 6, X-ray diffractograms are not clear above 25.0 wt% NaOHaq. This suggests that the chain packing of Na-Cell for (C) group is disordered due to the destruction of intramolecular hydrogen bonds, as in the discussion on the ^{13}C NMR spectra.

To consider these results from molecular motion, T_{1c} was measured for each carbon. Table I shows T_{1c} for each carbon for the (A), (B), and (C) groups. T_{1c} for each carbon for (A) group is longer than that in the original sample (Cell I). T_{1c} of the C_6 carbon in comparison with other carbons for (B) group is shorter than that of Cell I. It may be considered that a state of the molecular motion around the C_6 carbon as side chain changes because of the destruction of intermolecular hydrogen bonds. Each carbon's relaxation time for (C) group is shorter than that of Cell I. The molecular motion of the main chain may occur and chain packing may change to a disordered structure.

From these results, were drawn the following conclusions:

(1) $\text{O}_3\text{--H}\cdots\text{O}_5'$ intramolecular hydrogen bonds and $\text{O}_2\text{--H}\cdots\text{O}_6'$ intermolecular hydrogen bonds exist in the original sample (Cell I).

(2) The selective coordination of Na^+ to the hydroxyl group at C_2 is the most probable. By this selective coordination of Na^+ , the $\text{O}_2\text{--H}\cdots\text{O}_6'$ intermolecular hydrogen bond is broken.

(3) Above 25 wt% NaOHaq, the $\text{O}_3\text{--H}\cdots\text{O}_5'$ intramolecular hydrogen bond is broken by the selective coordination of Na^+ to O_3 at C_3 .

(4) Each carbon's spin-lattice relaxation time of Na-Cell for (B) and (C) groups becomes shorter than that of Cell I due to the destruction of intra- and intermolecular hydrogen bonds.

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