

Determination of Intramolecular Hydrogen Bonds and Selective Coordination of Sodium Cation in Alkalicellulose by CP/MASS ^{13}C NMR

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ABSTRACT: Alkalicellulose, prepared from wood pulp, was analyzed using CP/MASS ^{13}C NMR. In the alkalicellulose I solid, molecular motion is more rapid than that in the cellulose I solid and there is an intramolecular hydrogen bond between the hydroxyl at C_3 and ring oxygen O_5' , which is slightly weaker than that for cellulose I. A sodium ion was found to selectively coordinate to the hydroxyl oxygen at the C_2 position of the glucose unit.

KEY WORDS Alkalicellulose / CP/MASS ^{13}C NMR / Cellulose / Intramolecular Hydrogen Bond / Cellulose I /

Alkalicellulose is chemically highly reactive so that cellulose ethers, such as carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, ethylcellulose and their coethers, are at present commercially synthesized on a large scale *via* alkalicellulose as an intermediate compound from cellulose. Various crystal forms including alkalicellulose I, II, III, and IV have been found to exist by X-ray diffraction method and for each from the chemical composition of the sodium ion Na^+ , water and anhydrous glucose unit was determined by the chemical analysis.¹⁻⁴

It is widely recognized that the reactivity of alkalicellulose against other chemical reagent and the distribution of substituent groups of cellulose derivatives formed thus depend remarkably on the solid state structure (crystal form, crystallinity and morphology) of alkalicellulose. Alkalicellulose I (Nacell-I) readily reacts with carbon disulfide to give cellulose xanthate and the ratio of the probability of carboxymethylation at the hydroxyl group attached to C_6 position $\langle f_6 \rangle$, to that of total

degree of substitution $\langle F \rangle$ depends on the crystal form of the starting cellulose, if the operating conditions of carboxymethylation reaction are kept the same.⁵

However, there are unfortunately only few methods available to obtain directly detailed information on the chemical structure of cellulose solid. Wide-angle X-ray diffraction provides information only on the crystal structure.

Recently, we demonstrated that CP/MASS ^{13}C NMR technique is particularly useful to analyze the hydrogen bonds of a cellulose solid, and concluded that the intramolecular hydrogen bond plays an important role in the solubility of cellulose in dilute alkali.⁶ Applying the same technique to alkalicellulose, Kunze *et al.*^{7,8} demonstrated, although very qualitatively due to the low resolving of their NMR spectra, the change in the crystal form with alkali concentration.

In this article, an attempt is made to clarify, using CP/MASS ^{13}C NMR, whether the intramolecular hydrogen bond and selective coordination of Na^+ exist in Nacell-I, prepared by dipping cellulose I in a 18 wt%

aqueous sodium hydroxide solution.

EXPERIMENTAL

Cellulose

Wood pulp (C-1) having the viscosity-average molecular weight $M_v = 2.1 \times 10^5$ and crystal form of cellulose I was employed. Here, M_v was determined from the limiting viscosity number $[\eta]$ in cadoxen solution using Brown-Wikstrom's equation,⁹ $[\eta] = 3.85 \times 10^{-2} M_w^{0.76}$ at 25°C.

Alkalicellulose

A 100 weight part of cellulose was immersed in a 2000 weight part of a 18 wt% aqueous sodium hydroxide solution at 30°C for 30 min and then pressed between polyacrylonitrile cloth and cellulose filter paper by a hand press to give *ca.* a 280 weight part of alkalicellulose. Alkalicellulose thus prepared was referred to as AC-1. AC-1 was crushed in a mixer so that its apparent specific volume became 15 ml g⁻¹. AC-1 and stored in a closed vessel containing air at 49°C for 30 h. The sample thus aged was referred to as AC-1a.

CP/MASS ¹³C NMR

The NMR spectra were obtained on a JEOL FX-200 type FT-NMR spectrometer, using a cross polarization (CP)/dipole decoupled (DD)/magic angle sample spinning (MASS) technique: CP contact time 2 ms, repetition time 5 s, measuring temperature 50–80°C.

Sample code AC-1 was measured immediately after sample preparation and sample code AC-1a, after aging.

RESULTS

Figure 1 shows the CP/MASS NMR spectra of cellulose sample C-1 (Figure 1a), cited from the previous paper¹⁰ and of its alkali celluloses

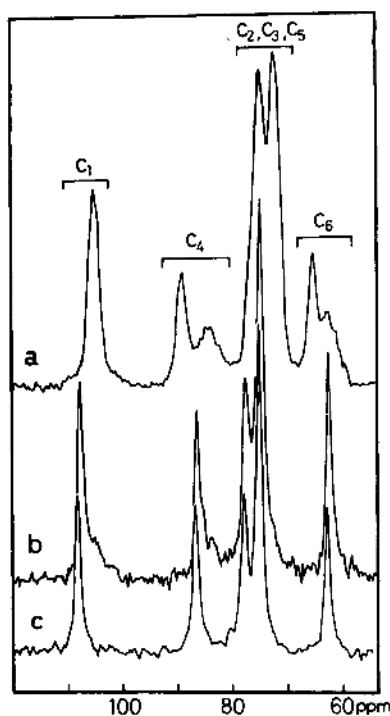


Figure 1. CP/MASS ¹³C NMR spectra of cellulose I and alkalicelluloses. a, cellulose I (C-1); b, alkalicellulose without aging (AC-1); c, aged alkalicellulose (AC-1a).

Table I. Peak assignment of cellulose and alkali cellulose

Samples	Carbon position/ppm							
	C ₁		C ₄		C ₂ , C ₃ , C ₅		C ₆	
C-1	105.4 ^b (1.00)		89.1 (0.47)	84.5 ^b (0.53)	75.3 (1.57)	72.2 (1.51)	65.5 (0.55)	63.0 ^b (0.38)
AC-1	107.8 (1.00)	105.3 ^s	86.4 (0.71)	85.4 ^s (0.29)	83.8 ^b (0.98)	77.7 (2.10)	74.9 (0.98)	62.8 (0.98)
AC-1a	108.3 (1.00)		86.8 (1.02)			78.0 (1.10)	75.1 (2.10)	63.0 (0.98)

b denotes broad peak, s, shoulder peak and the value in parenthesis are peak intensities.

AC-1 and AC-1a (Figures 1b and c, respectively). Table I shows the peak positions (TMS as reference material) and integrated peak intensity (in blanket) of NMR spectra in Figure 1. Suffix b refers to a broad peak.

The half-value width of all NMR peaks of alkalicellulose was only 1/2—1/4 that of cellulose. The peak positions of cellulose were almost similar with those for alkalicellulose. Peaks at 108, 90—80, and 63 ppm were assigned for C_1 , C_4 , and C_6 carbons. In Figure 1, the C_1 and C_4 carbon peaks for AC-1a are seen as singlet at 108.3 and 86.3 ppm, respectively. But AC-1 sample has a small higher field component in both the C_1 and C_4 carbon peak regions, showing AC-1a have weaker parts in intramolecular hydrogen bonding compared with that of AC-1.

DISCUSSION

From Figure 1, it is obvious that the C_4 and C_6 carbon peaks for cellulose show broad distribution depending on the wide distribution of the bond strength of the intramolecular hydrogen bond (Figure 1a). In contrast, all carbon peaks for alkalicellulose are simple and sharp (Figures 1b and 1c). This is particularly apparent in AC-1a. This strongly suggests that in alkalicellulose, the distance between molecular chains is so widened due to swelling action of alkali against cellulose that as many conformations of glucoside linkage as that in solution are possible and the rate of interconversion of these conformations is relatively rapid. This leads to a single and sharp time-averaged NMR peak (*i.e.*, AC-1a) due to each carbon's relaxation time. In this sense, alkalicellulose has the uniform solid structure. Each carbon peak position does not always coincide with that for cellulose dissolved in aq. sodium hydroxide. The C_4 carbon peak in solution, where $\text{O}_3\text{-H} \cdots \text{O}_5'$ intramolecular hydrogen bonds are considered to be completely broken, resonates at *ca.* 80 ppm,⁶ and the corresponding peak, originating from the

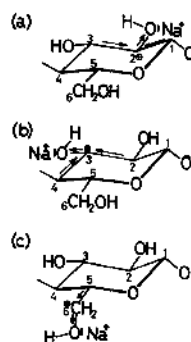


Figure 2. Possible chemical structure of alkalicellulose. Alkalicellulose with selective coordination of a sodium ion to the hydroxyl oxygen at the C_2 (a), C_3 (b), and C_6 (c) positions; arrow mark denotes location of electron.

region in which the intramolecular hydrogen bonds are strongly formed, is observed at 89 ppm. The C_4 carbon peak of alkalicellulose is observed at 86—87 ppm. These experimental facts show that even in alkalicellulose, there exist weak intramolecular hydrogen bonds.

C_1 carbon peak of cellulose varies between 104 and 106 ppm, depending on the strength of $\text{O}_3\text{-H} \cdots \text{O}_5'$ intramolecular hydrogen bonds.¹⁰ Unexpectedly, the C_1 carbon peak of alkalicellulose is sharp at 108 ppm and significantly outside the possible variation of the C_1 carbon peak of cellulose. This must be explained on a basis other than the intramolecular hydrogen bonding. This situation is the same for the peak at 78 ppm for alkalicellulose. To explain the appearance of this peak, the abstraction of an electron from the carbon adjacent to the hydroxyl group, induced by selective coordination of Na^+ to the hydroxyl group, should be considered. As is well-known, alkalicellulose I has the chemical composition of $\text{C}_6\text{H}_{10}\text{O}_5 \cdot \text{NaOH} \cdot 3\text{H}_2\text{O}$, meaning that Na^+ is coordinated to a glucose ring. Figure 2 shows the possible chemical structure of alkalicellulose I when Na^+ is selectively coordinated to the hydroxyl groups at C_2 , C_3 , and C_6 , respectively. Whether the states shown in Figure 2 are stable as alcoholates is not clear, but the electron density on the carbons located at

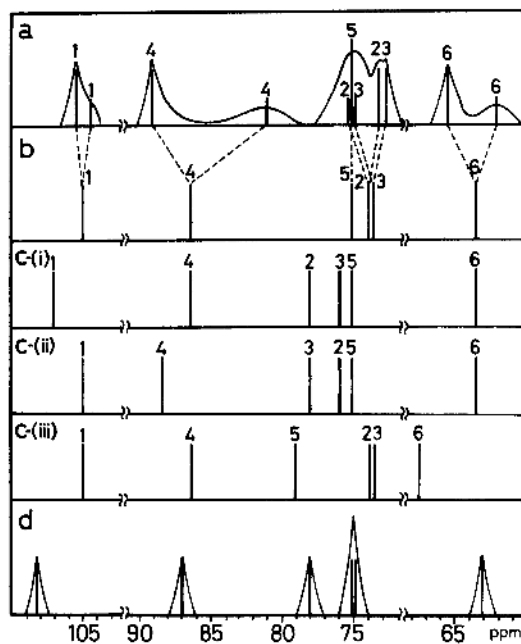


Figure 3. Schematic representation of CP/MAS ^{13}C NMR spectra. a, cellulose I experimentally observed; b, alkalicellulose when selective coordination of the sodium ion does not occur; c-(i), alkalicellulose with selective coordination of the sodium ion at C_2 ; c-(ii), alkalicellulose with selective coordination of the sodium ion at C_3 ; c-(iii), alkalicellulose with selective coordination of the sodium ion at C_6 ; d, aged alkalicellulose (AC-1a), experimentally observed.

the α and β positions from the hydroxyl groups selectively coordinating with Na^+ must diminish. Thus, the α and β carbon NMR peaks must shift towards a lower magnetic field, compared with the corresponding carbon peaks when the above-mentioned selective coordination of Na^+ is not considered. Of course, the degree of cationization of α carbon is larger than that of β carbon. For the form (a) shown in Figure 2, C_2 carbon might be considerably cationized as well as the C_3 carbons. In this connection, the degree of cationization of C_1 carbon is larger than that of the C_3 carbons, because in alkalicellulose, the remaining $\text{O}_3\text{-H} \cdots \text{O}_5'$ intramolecular hydrogen bonding, before-mentioned, may anionize the C_3 carbon. By analogy, for the

form (b), the C_3 carbon is considerably cationized and C_2 and C_4 , slightly cationized. For the form (c), the C_6 and C_5 carbons are cationized. Thus, corresponding to the forms shown in Figure 2, the C_1 , C_2 , C_3 , C_4 , C_5 and C_6 carbon NMR peaks must shift towards a lower magnetic field, compared with the corresponding carbon peaks when the above-mentioned selective coordination of Na^+ is not considered. Figure 3a shows a schematic representation of the CP/MAS ^{13}C NMR spectrum of cellulose I, experimentally determined and Figure 3b shows a hypothetical spectrum of alkalicellulose I having an $\text{O}_3\text{-H} \cdots \text{O}_5'$ intramolecular hydrogen bond when the effect of the coordination of Na^+ is not considered. Figure 3c-(i), (ii), and (iii) show hypothetical line spectra of alkalicelluloses, having the chemical structure shown in Figure 2a, b, and c, respectively. A comparison of these spectra with the spectrum in Figure 3b, shows 1) the C_1 , C_2 , and C_3 carbon peaks to be located in lower magnetic fields when Na^+ coordinates to the hydroxyl group at C_2 position (Figure 3c-(i)), 2) all C_2 , C_3 , and C_4 carbon peaks for alkalicellulose when Na^+ is assumed to coordinate to the hydroxyl group at C_3 position to shift towards a lower magnetic field (Figure 3c-(ii)), and 3) the C_5 and C_6 carbon peaks also to shift towards a lower magnetic field when Na^+ coordinates to the hydroxyl group at the C_6 position (Figure 3c-(iii)). The degree of this shift is expected to be greater for α carbons than β carbons. Figure 3d shows a schematic spectrum, experimentally observed for sample AC-1a. A comparison of Figure 3d with Figure 3c-(i), (ii), and (iii) indicates that selective coordination of Na^+ to the hydroxyl group at C_2 (Figure 2a) is the most probable.

Summarizing, in an aged alkali cellulose solid, the molecular motion is relatively rapid, as compared with a cellulose solid and has intramolecular hydrogen bondings and a sodium ion selectively coordinates to the hydroxyl oxygen at the C_2 position of cellulose.

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