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NOTE

Determination of Distribution of Sodium Sulfate Group in Glucopyranose Units of Sodium Cellulose Sulfate by ^{13}C and ^{1}H Nuclear Magnetic Resonance Analysis

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In cellulose derivatives, the hydroxyl groups attached at the C_2, C_3, and C_6 positions in glucopyranose units making up a cellulose chain are partly or fully substituted with other functional groups such as nitrate, acetate, and sulfate groups. Therefore, the physical and chemical properties of these derivatives are, as expected, governed by the overall distribution of such functional groups in the C_2, C_3, and C_6 positions and these groups are designated as $\langle\langle f_2 \rangle\rangle$, $\langle\langle f_3 \rangle\rangle$, $\langle\langle f_6 \rangle\rangle$ and the total degree of substitution is termed $\langle\langle F \rangle\rangle$ ($=\langle\langle f_2 \rangle\rangle+\langle\langle f_3 \rangle\rangle+\langle\langle f_6 \rangle\rangle$). Here, $\langle\langle f_k \rangle\rangle$ ($k=2$, 3, and 6) is the probability of substitution of hydroxyl group attached to the C_k position, averaged over all glucopyranose rings belonging to all the molecules in a sample. In a previous paper,[1] we developed a new method for derermining $\langle\langle f_k \rangle\rangle$ ($k=2$, 3, and 6) for *O*-acetyl groups in cellulose acetate by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) methods. In this paper, as an extension of the previous work,[1] an attempt is made to evaluate $\langle\langle f_k \rangle\rangle$ as well as $\langle\langle F \rangle\rangle$ for sulfate groups in sodium cellulose sulfate (NaCS) by ^{1}H and ^{13}C NMR methods.

Purified cotton lint was hydrolyzed with 1.0 mol aqueous sulfuric acid at 60°C for 6 h to give a cellulose sample having a viscosity-average molecular weight, $M_v=0.9\times10^4$. NaCS was synthesized by reacting cellulose with sulfur trioxides–dimethylformamide (DMF) complex at 10°C according to the method proposed by Schweiger,[2] and this was followed by the addition of sodium hydroxide. NaCS thus prepared was redissolved in water to give a solution of 5 g dl^{-1}, dialyzed with purified water until the electroconductivity of the dialysate became below 1×10^{-5} Ω^{-1} cm^{-1}, and dried *in vacuo*. The NaCS sample had a viscosity-average molecular weight, $M_v=1.5\times10^4$, which was determined by putting the limiting viscosity number $[\eta]$ ($=544$) in a 0.5 mol aqueous NaCl solution at 25°C into the Mark–Houwink–Sakurada equation: $[\eta]=7.91\times10^{-2}$ $M_w^{0.93}$,[3] $\langle\langle F \rangle\rangle$ was determined by chemical analysis[2] (method of gravimetric analysis by converting sulfuric group into barium sulfate following decomposition of NaCS with hydrochloric acid), and was found to be 1.96.

The ^{1}H and ^{13}C NMR spectra (100 MHz) of the NaCS solution in deuterium oxide (D_2O) were obtained by a JOEL FX 100 Pulse-Fourier Transform NMR spectrometer at 37°C. The detailed operation conditions are briefly summarized as follows.

For ^{1}H NMR: pulse width, 15 s; pulse angle, 90°; interval 3.41 s; multi-pulse (8), 4095 times data accumulation; WEFT (water elimination) mode for integrated peak intensity.

For ^{13}C NMR: dioxane was added in order to eliminate the Overhauser effect, ^{1}H-decouple mode. Internal reference was sodium 2, 2-dimethyl-2-silapentane-5-sulfonate

Figure 1 demonstrates all three differently sulfonated anhydroglucose units of NaCS with $\langle\langle F \rangle\rangle=2.00$. Figure 2 shows ^{13}C NMR spectrum in

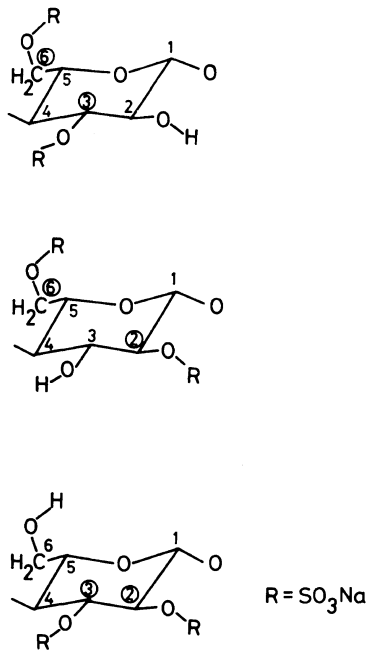

Figure 1. Possible conformation of glucopyranose units in sodium cellulose sulfate (《F》=2.0). Numbers denote positions of carbon atoms, to which a non-substituted hydroxyl groups are attached, constituting the glucopyranose units. Numbers in circle denote positions of carbon atoms, to which substituted hydroxyl groups are attached.

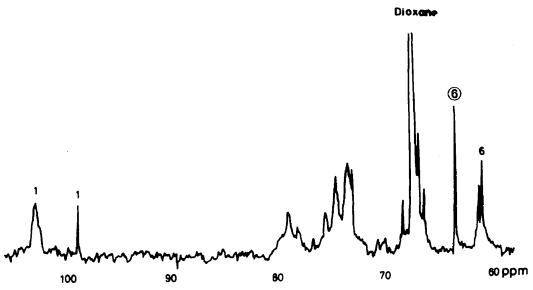

Figure 2. ^{13}C NMR spectrum of NaCS (《F》=1.96) in deuterium oxide. Numbers and symbols are the same as described in Figure 1.

D_2O. Carbons at the C_2–C_5 positions yield complicated peak signals at 70—80 ppm, from which neither 《f_2》 nor 《f_3》 could be directly estimated. C_6 carbon gave three peaks at 63.4, 61.2, and 60.8 ppm. Since the deshielding effect due to sulfate groups is expected to be almost equivalent to that of the acetyl group, the peak at 63.4 ppm could be

Table I. Chemical shift and assignment of the peaks in ^{13}C NMR spectrum of sodium cellulose sulfate

《F》 by chemical analysis	Chemical shift/ppm		
	C_1	C_2—C_5	C_6
1.96	103.1, 102.7, 99.3	79.2, 78.0, 75.6, 74.7, 73.6, 73.2	63.4, 61.2, 60.8

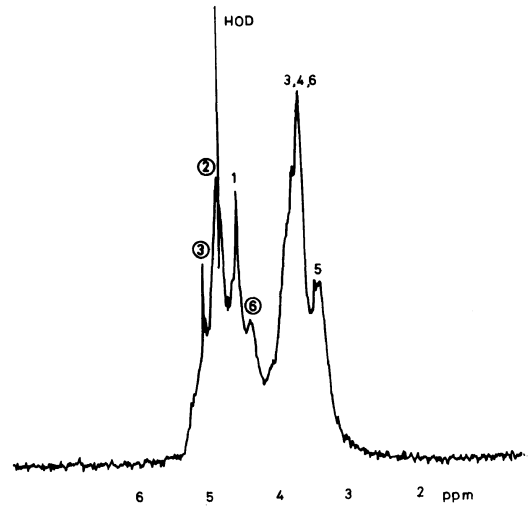

Figure 3. ^1H NMR spectrum of NaCS (《F》=1.96) in deuterium oxide. Numbers and symbols are the same as described in Figure 1.

attributed to the C_6 carbon bearing the sulfate group. The peak signal at 60.8 ppm is considered due to the unsubstitute-*d* C_6 carbon. The peak at 61.2 ppm may be assigned to either the unsubstituted C_6 carbon (hypothesis A) or the C_6 carbon bearing free sulfate group ($-OSO_3H$) (hypothesis B). The 《f_6》 value differs in regard to the assignment of the 61.2 ppm peak signal, which was found to be 0.34 for hypothesis A and 0.44 for hypothesis B from the area under peaks. In Table I, chemical shift and assignment of the peaks of ^{13}C NMR spectrum are presented. Three peaks at 103.1, 102.7, and 99.4 ppm are assigned to the C_1 carbon, which was employed by Wu[4] for estimating 《f_2》 and 《f_3》 of the nitrate group. But in this case, these peaks cannot be used for estimating 《f_2》 and 《f_3》 due to lack of sufficient knowledge about the shielding

effect of sulfate groups in the C_2 and C_3 positions. Of course, the integrated intensity of the C_1 carbon region was nearly equal to that of the C_6 carbon region.

Figure 3 shows the corresponding ^1H NMR spectrum of NaCS solution in D_2O. OH groups from NaCS were all converted into OD groups. Peak assignment was performed by a mutual comparison of a peak areas, and a comparison of the spectrum with that of cellulose acetate.[5] The proton signal at the C_3 position, which was sulfated, appears at the lowest magnetic field strength (4.97 ppm). Side band from HOD may be included to a small degree in peaks 3 and 1. In Table II, the chemical shifts, assignments, and intensities of the peaks are shown together. Thus, $\langle\langle f_2 \rangle\rangle$, $\langle\langle f_3 \rangle\rangle$, and $\langle\langle f_6 \rangle\rangle$ can be accurately evaluated from ^1H NMR spectrum alone within an accuracy of ± 0.030, 0.035, and 0.012, respectively by the following equations.

$$\langle\langle f_2 \rangle\rangle = \frac{7I_2}{\sum_{i=1}^{6} I_i} \quad (1)$$

$$\langle\langle f_3 \rangle\rangle = \frac{7I_1}{\sum_{i=1}^{6} I_i} \quad (2)$$

$$\langle\langle f_6 \rangle\rangle = \frac{7I_4/2}{\sum_{i=1}^{6} I_i} \quad (3)$$

where I_1, I_2, I_3, I_4, I_5, and I_6, are the integrated peak intensities at 4.97, 4.83, 4.56, 4.39, 4.0—3.5, and 3.42 ppm respectively. Equation 3 was derived assuming that the proton directly attached to the substituted C_6 position is not contaminated in the integrated peak intensity I_3. The validity of this assumption is confirmed by,

$$\frac{7I_3}{\sum_{i=1}^{6} I_i} = 1.00$$

Putting the data in Table II into eq 1—3 give $\langle\langle f_2 \rangle\rangle = 1.00$, $\langle\langle f_3 \rangle\rangle = 0.61$, and $\langle\langle f_6 \rangle\rangle = 0.34$. The latter value (0.34) is in good agreement with that (0.34) evaluated with hypothesis A. This confirms the validity of the assignments proposed for the ^{13}C NMR spectrum. In addition, from the $\langle\langle f_k \rangle\rangle$ data by ^1H NMR, we obtain $\langle\langle F \rangle\rangle = 1.95$, which agrees well with that of the chemical analysis.

The C_1 proton signals in ^1H NMR spectra possibly overlap with the proton signals of the C_6 position bearing sulfate group should the C_6 position be highly substituted, thus making evaluation of $\langle\langle f_6 \rangle\rangle$ by ^1H NMR analysis difficult. Even in this case, $\langle\langle f_k \rangle\rangle$ can be determined by the following procedure.

(1) determination of $\langle\langle F \rangle\rangle$ by chemical analysis

(2) determination of $\langle\langle f_2 \rangle\rangle$ and $\langle\langle f_3 \rangle\rangle$ using eq 1 and 2.

(3) determination of $\langle\langle f_6 \rangle\rangle$ by

$$\langle\langle f_6 \rangle\rangle = \langle\langle F \rangle\rangle - (\langle\langle f_2 \rangle\rangle + \langle\langle f_3 \rangle\rangle) \quad (4)$$

Table II. Chemical shift, assignment, integrated peak intensity, and $\langle\langle f_k \rangle\rangle$ of ^1H NMR spectrum for sodium cellulose sulfate in deuterium oxide

$\langle\langle F \rangle\rangle$		Chemical shift	Assignment	Peak intensity	$\langle\langle f_k \rangle\rangle$
Chemical analysis	^1H NMR	ppm			
1.96	1.95	4.97	H_3 proton[a]	$I_1 = 16.2$	0.61
		4.83	H_2 proton[a]	$I_2 = 26.7$	1.00
		4.56	H_1 proton	$I_3 = 26.7$	—
		4.39	H_6 proton[a]	$I_4 = 18.0$	0.34 (0.34)[b]
		4.0—3.5	H_3, H_6, H_4 protons	$I_5 = 72.0$	—
		3.42	H_5 protons	$I_6 = 26.7$	—

[a] Signals of protons attached to C_k ($k = 2$, 3, and 6) position bearing a sulfate group.
[b] By ^{13}C NMR.

The reactivity of hydroxyl groups at the C_2, C_3, and C_6 positions of cellulose with the SO_3–DMF complex decreased in the following order: $C_2 > C_3 > C_6$. If the hydrolysis reactions of NaCS are assumed to be the reverse of the order mentioned above, then the hydrolysis of the substituent at C_2 is the lowest. This clearly contradicts the fact that the reactivity of *O*-acetyl groups in cellulose acetate with hydrochloric acid, previously evaluated, is of the order: $C_2 > C_6 > C_3$. This means that the reactivity of hydroxyl or substituents of cellulose or its derivatives cannot be primarily predicted according to position alone.

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