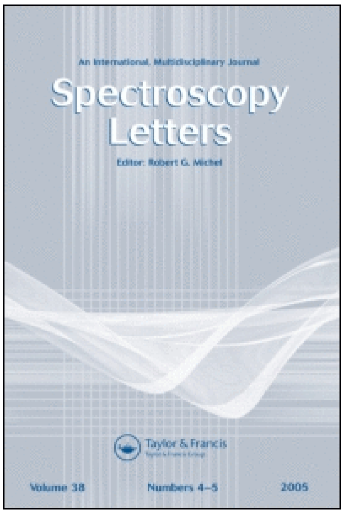

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DETERMINATION OF THE MOLAR SUBSTITUTION OF HYDROXYPROPYL CELLULOSES BY AN NMR METHOD

Keywords: Hydroxypropyl cellulose; ^{1}H-nmr; hydrolysis; molar substitution

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ABSTRACT

Proton nuclear magnetic resonance (^{1}H-nmr) techniques have been used for the determination of the molar substitution (MS) of hydroxypropyl cellulose. The method for measuring MS was based on the hydrolysis of hydroxypropyl cellulose with concentrated deuteriochloric acid (DCl) and integration of area of the nmr peaks of the hydrolyzed product. The results obtained by the proposed nmr method agreed well with those provided by the chromic acid oxidation distillation method. Furthermore, according to the established relationship between average MS and the content of hydroxypropyl group (HC), the MS of hydroxypropyl cellulose was also calculated, and therefore further verifying the accuracy of the nmr data.

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INTRODUCTION

Hydroxypropyl cellulose, which contains methyl, methylene, methyne hydroxypropyl groups, has many practical applications in medicine and industrial fields, it is therefore often desired to determine the molar substitution (MS) and degree of substitution (DA) per hydroglucose unit, two of the important chemical parameters of the cellulose. Chromic acid oxidation-gas chromatography procedures for ethoxy content of ethylcellulose was traditionally used for the purpose [1]. Proton magnetic resonance has also been reported to measure the MS of cellulose ether [2]. Lee et al. [3,4] and Lbbett [5] studied on the distribution substituents and thermal behavior of cellulose by using carbon-13 nmr spectroscopy. This paper describes a method for the determination of the MS of hydroxypropyl cellulose by using ^{1}H-nmr data. Several kinds of hydroxypropyl celluloses which were synthesized in our laboratory were measured to testify the proposed method.

EXPERIMENTAL

The nmr spectra were recorded with a Varian FT-80A spectrometer operated at 79.54 MHz in standard 5-mm o.d. glass tubes. Pulse width was 50 μs ($\pi/2$ pulse angle) and repetition time was set 10 s. The signal intensities were obtained from a computer print-out, as well as from the measurements of the area of scale-expanded signals. Chemical shifts (δ) in ppm referenced to the internal calibrant 2,2-dimethyl-2-silico-pentane-5-sulfonate sodium (DSS).

A series of samples containing hydroxypropyl celluloses were synthesized in our laboratory according to the procedures reported in Pef. [6], details of which are listed in Table 1. The samples were weighed precisely and placed into an nmr tube, ca. 0.3 ml of reagent grade concentrated DCl (deuterium content >99%) was then added. The mixture was agitated to disperse the cellulose, the tube was then placed in a water bath at about 50℃ for 1-2 h. After hydrolysis reaction took place, an appropriate amount of D_2O was added into the nmr tube for locking field and the spectra were thus measured.

Table 1 Hydroxypropyl contents of the samples tested and MS data of the hydropropyl group measured by different methods (measured after hydrolysis at 50°C)

Sample	Hydroxypropyl content (%)	MS by Proposed Method Hydrolysis time (h) 1	 2	MS by Chemical Method	MS from Eq (4)
1	7.70	0.185	0.224	0.190	0.233
2	10.0	0.225	0.310	0.270	0.316
3	12.7	0.328	0.397	0.360	0.406
4	22.8	0.630	0.767	0.730	0.825
5	29.2	0.870	1.04	0.960	1.15
6	37.4	1.31	1.45	1.32	1.67
7	49.0	1.96	2.24	2.21	2.68

RESULTS AND DISCUSSION

One typical schematic structure of hydroxypropyl cellulose is illustrated in Fig. 1. The nmr spectra of hydroxypropyl cellulose for Sample 1, are shown in Fig.2, of which (a) was run immediately after dissolution in DCl at ambient temperature (this took ca. 30 min) and (b) was run once more after 2 h at 50°C.

In Fig. 2 (a), a doublet at high field (1.13, 1.24 ppm from internal DSS reference) can be readily assigned to the methyl protons, and the strong single peak at 2.16 ppm is referred to the methyl protons of diluent toluene. When other diluents were used, the peak disappeared. The broad peak from 3.62 to 3.89 ppm (center) results from methylene and methyne protons, excluding the proton of carbon-1. The peaks of the proton of the carbon-1 in backbone appears at 4.53 ppm, being at the field lower than that of the other bands; this is because that carbon is bonded to two oxygen atoms, whereas the other carbon atoms are bonded with only one. The hydroxyl proton exchanges with the HCl-HDO hydrogen, contributing to a strong labile-hydrogen resonance near 7.56 ppm. From Fig. 2 (b), we can see that the peak at 4.53 ppm disappeares, while the peaks at the region between 4.77 and 5.34 ppm represente the proton of carbon-1 and the labile hydrogen chemical shift moves to ca. 7.06 ppm, thus, indicating that the hydrolysis reaction had completed.

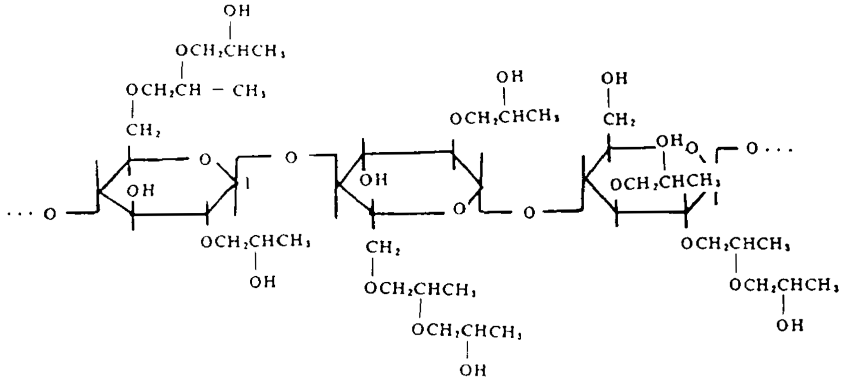

Fig.1 A possible structure of hydroxypropyl cellulose

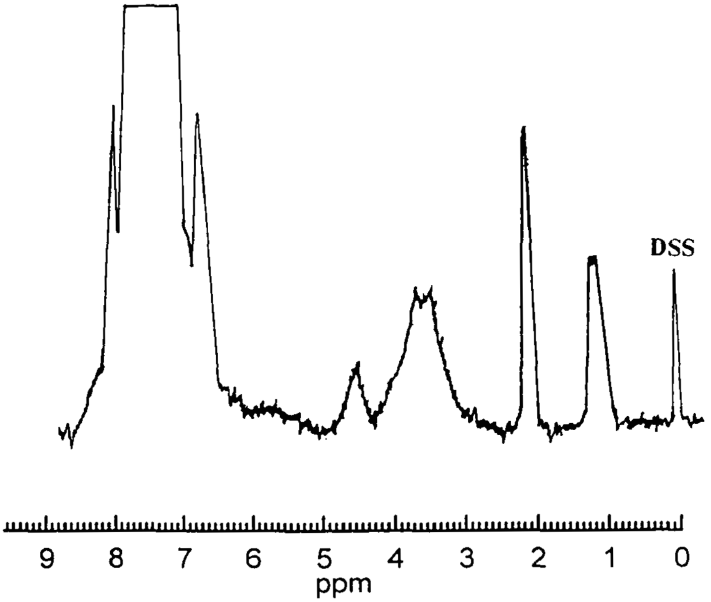

Fig.2 (a) Spectrum obtained immediately after dissolution in DCL

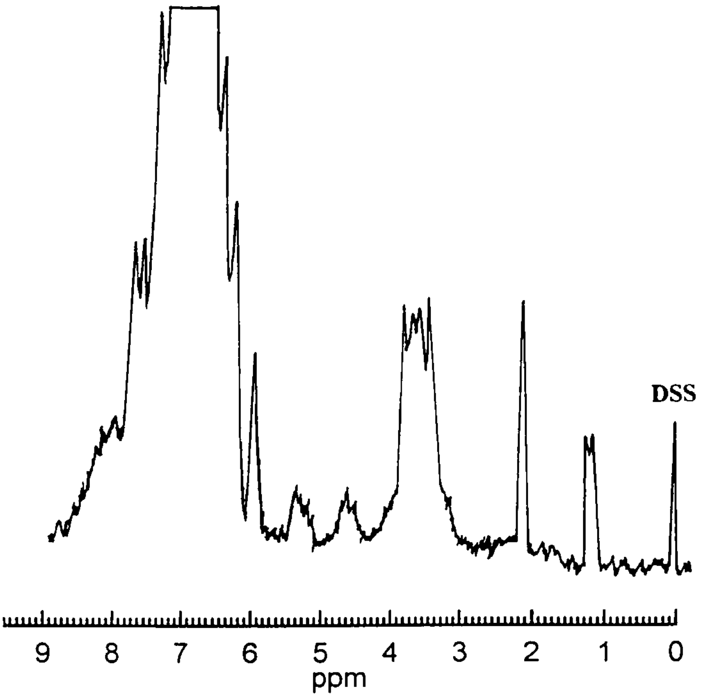

Fig.2 (b) Spectrum after 2 hours at 50℃

As shown seen in Fig. 1 and Fig.2, if the integrated area from methyl protons is referred as C, and the area from methylene and methyne protons as B, the total area under the 4.77-5.34 ppm bands as A (corresponding to one proton), then, the MS of hydroxypropyl cellulose can readily be calculated by

$$\frac{C}{A+B}=\frac{3MS}{1+(3MS+6)} \qquad (1)$$

In equation (1), the number *3* represents the three hydroxypropyl of each hydroglucose unit, and the *1*, *6* refer to the proton of carbon-1 and others except for hydroxypropyl protons, respectively. From equation (1), following equation can be obtained:

$$\mathrm{MS}=\frac{7C}{3(A+B-C)} \qquad (2)$$

The relationship between MS and content of hydroxypropyl group (HC) could be formulated as

$$HC = \frac{58MS}{162 + 58MS} \times 100\% \qquad (3)$$

where the molar weight of hydroxypropyl is *58*, and the value of *162* represents the molar weight of hydroglucose unit. Equation (3) can be furthermore reformulated as

$$MS = \frac{162HC}{58(100 - HC)} \qquad (4)$$

For the proton nmr spectra, if the pulse decay time is greater than or equals to $5T_1$ (T_1 refers to spin-lattice relaxation time), the integral area of peak is in proportional to the population [7]. The molar substitutions of hydroglucose unit for seven samples measured by proton nmr spectra are listed in Table 1.

The data in Table 1 indicate that the shorter the hydrolysis time, the smaller the average MS of hydroxypropyl, this is believed to be a result of the uncompleted hydrolysis. The average MS values of hydroxypropyl measured by ^{1}H-nmr are generally lower than the values calculated from Equation (4), this is because of the following two factors: (1) hydrolysis of hydroxypropyl cellulose is normally incomplete, and (b) the relaxation time of the terminal methyl is larger than other protons, thus, when the radio-frequency field is applied, the magnetization of methyl proton cannot be recovered to the equilibrium scale during the 10 seconds period; this result in the integral area of methyl protons become lower and the errors may arise.

In order to verify the accuracy of the proposed nmr method, a chromic acid oxidation distillation [8] has been used to analyze the samples, the results are also listed in Table 1 for comparison. From the data listed in the table, we can conclude that the nmr data are compared favorably with that of the standard chemical method.

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