A Further Study on Solvation in Cellulose Triacetate Solutions by Pulse-Fourier ^1H and ^{13}C NMR Method

Kenji KAMIDE, Masatoshi SAITO, Keisuke KOWSAKA,
and Kunihiko OKAJIMA

*Fundamental Research Laboratory of Fiber and
Fiber-Forming Polymers, Asahi Chemical Industry Co., Ltd.,
11-7, Hacchonawate Takatsuki, Osaka 569, Japan*

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ABSTRACT: An attempt was made by pulse-Fourier ^1H and ^{13}C NMR to measure the chemical shift δ of the *O*-acetyl-methyl (AMH) and -carbonyl carbon (ACC) of cellulose triacetate (CTA, the total degree of substitution $\langle F \rangle = 2.92$) in various deuterated solvents and to determine whether the possibility of the solvation depends on the position (C_2 , C_3 , or C_6) of the *O*-acetyl group or not and if so, to evaluate the positions of the *O*-acetyl group, to which the solvent molecules are preferentially solvated. Among *N,N*-dimethylsulfoxide (DMSO), pyridine (Py), trichloromethane (TCM) and acetone, the spin-lattice relaxation time of AMH at C_2 carbon and that of ACC at C_2 , C_3 , and C_6 carbons were maximum in acetone, indicating that acetone molecules interact the most weakly with *O*-acetyl group. The difference of δ of AMH at each carbon position (C_2 , C_3 , and C_6) between DMSO or Py or TCM and acetone was positive in DMSO and negative in Py, TCM. The similar difference of δ of ACC was always positive, except the case of ACC at C_2 and C_3 positions in Py, where the difference was zero. Assuming no specific interaction between acetone and CTA we can conclude that DMSO and TCM molecules solvate equally with *O*-acetyl group at C_2 , C_3 , and C_6 positions, but the pyridine molecule solvates only with *O*-acetyl group at C_6 position.

KEY WORDS Cellulose Triacetate / FT-NMR / Chemical Shift / Solvation
/ Methyl Proton / Carbonyl Carbon /

The earliest study of the interaction between the cellulose derivative and the solvent molecule (*i.e.*, the solvation) seems to have been that of Moore and his coworkers,¹ who in 1965 measured the adiabatic compressibility of solutions of cellulose acetate (CA), cellulose nitrate, ethylcellulose and so on, estimating the number of the solvent molecules solvated to a glucopyranose ring, s . Unfortunately, as Kamide and Saito² pointed out later, the accuracy and preciseness of their data on the sound velocity are not satisfactory. Recently Kamide *et al.*³ found from the measurements of ^1H NMR chemical shifts δ of the hydroxyl- and *O*-acetyl methyl protons of CA with the total degree of substitution $\langle F \rangle = 0.49$ — 2.92

that (1) there exists the solvation of solvent molecules to *O*-acetyl and hydroxyl groups, (2) δ becomes larger in polar solvents, and (3) δ of the hydroxyl proton attains maximum at $\langle F \rangle \simeq 2.5$ in *N,N*-dimethylacetamide (DMAc). Successively Kamide and Saito² measured the adiabatic compressibility of solutions of CA samples and concluded that s at infinite dilution, s_0 ($\equiv \lim_{c \rightarrow 0} s$, c is the concentration) depends on the solvent nature in the same manner as δ . The strong relationships of s_0 with the unperturbed chain dimension A and the partially draining parameter X^{4-8} were experimentally demonstrated for CA with $\langle F \rangle = 0.49$ — 2.92 in various solvents. These

experimental facts indicate explicitly that the solvation plays predominant roles in the flexibility of the unperturbed chain together with the hydrodynamic interaction in CA solutions. In other words, it is considered that the solvated solvent molecule yields a significant steric hindrance and an interaction between the solvated and free solvent molecules results in partial free drainage. It is natural to conceive that the solvent molecules possibly solvate to different extents with the *O*-acetyl or hydroxyl groups at three different carbons (*i.e.*, C₂, C₃, and C₆) in a glucopyranose unit.

If the above reasoning is unconditionally acceptable, the difference in the position of the *O*-acetyl and/or the hydroxyl group, to which the solvent molecules are solvated, is expected to cause a different effect on *A* and *X*. A recent commercialization of Fourier-transform (FT)-NMR makes it possible to evaluate the intensity of the solvation.

In this article as an extension of our earlier work³ we measure the chemical shift δ and the relaxation time T_1 by FT-¹H and -¹³C NMR for cellulose triacetate (CTA) in various solvents to disclose the solution structure of CTA-solvent system.

EXPERIMENTAL

Polymer Sample and Solvents

A CTA whole polymer with $\langle F \rangle = 2.92$ (the weight-average molecular weight $\bar{M}_w = 2.32 \times 10^5$ and the number-average molecular weight $\bar{M}_n = 5.85 \times 10^4$), employed in the previous papers^{2,3,9} was used for NMR measurements. Deuterated trichloromethane (TCM)-*d*₁, pyridine (Py)-*d*₅, acetone-*d*₆, *N,N*-dimethylsulfoxide (DMSO)-*d*₆, and DMAc-*d*₉ were used as received from the manufacturer (E. Merck, Darmstadt, FRG).

¹H and ¹³C NMR Measurements

The CTA sample, dried *in vacuo* at 40°C for 24 h, was mixed with solvents except acetone to give 7 wt% solution in the NMR sample

tube. For TCM and DMAc the dissolution was carried out at room temperature with 20 min mixing and for pyridine and DMSO the tube was placed in an NMR cell and the solution was prepared at 120°C by rotating the tube at a rate of 20 rpm. The mixture of the CTA sample flake and acetone was quenched to -170°C, maintained at that temperature for 1 h and the clean and transparent solution of 3 wt% CTA was obtained by raising the temperature of the mixture very gradually to room temperature.

δ values of the *O*-acetyl methyl proton (AMH) and *O*-acetyl carbonyl carbon (ACC) were determined on a FX-200 JEOL FT-NMR spectrometer (Japan Electron Optics Laboratory Co., Tokyo) using tetramethylsilane (TMS) as a reference. ¹H NMR spectra were obtained under the following conditions: Frequency 199.5 MHz, pulse width 45° (7 μ s), repetition time 8 s, data points 16384, accumulation 16 times. Only for CTA-acetone system, 180- τ -90° (τ , pulse interval) pulse was used to eliminate peak of acetone having long spin-lattice relaxation time T_1 (in this case, $\tau = 5$ s, repetition time 30 s). ¹³C NMR spectra were obtained under the following conditions: Frequency 50.15 MHz, pulse width 45° (6.5 μ s), repetition time 3.2 s, complete decoupling of ¹H nuclei. For acetone, DMSO and pyridine the solvent peaks overflowed by frequency domain accumulation. The repetition was *ca.* 1000–4000 times. T_1 was measured by the inversion recovery method using 180- τ -90° pulse sequence.

RESULTS AND DISCUSSION

Figure 1 shows the ¹H NMR spectra of the *O*-acetyl methyl proton region of CTA in five deuterated solvents. Generally, three peaks were observed for the *O*-acetyl methyl proton. δ of these peaks varied over the wide range of 1.8–2.2 ppm. The intensity ratio in TCM, calculated from the peak area, is 0.99:1.04:1.00 for three peaks at 1.95, 2.00,

Figure 1. ^1H NMR spectra of cellulose triacetate ($\langle F \rangle = 2.92$) in various deuterated solvents in *O*-acetyl methyl proton region. a) DMAc- d_6 ; b) DMSO- d_6 ; c) acetone- d_6 ; d) pyridine- d_5 ; e) TCM- d_1 .

and 2.12 ppm. Up to now ^1H NMR measurements on CTA with $\langle F \rangle > 2.9$ were without exception carried out on 100 or less MHz NMR spectrometers, which have less resolved power for this purpose. Goodlett *et al.*¹⁰ assigned, from a comparison of the reactivity of three hydroxyl groups at C_2 , C_3 , and C_6 positions with toluene-sulfonyl chloride, three peaks at 1.94, 1.99, and 2.09 ppm for CTA in TCM to be the *O*-acetyl methyl protons at the C_3 , C_2 , and C_6 position, respectively. Shiraishi and his coworkers¹¹ arrived at the same conclusion as Goodlett *et al.* by studying the correlations between the acidity of *O*-acetyl methyl groups at C_2 , C_3 , and C_6 positions and their electron deshielding effect and by estimating the degree of shift of the methyl proton peak of CTA in TCM to a lower magnetic field. The intensity ratio

of these three peaks corresponds accurately to the degree of substitution of three hydroxyl groups at C_3 , C_2 , and C_6 positions with the acetyl group (*i.e.*, $\langle f_3 \rangle$, $\langle f_2 \rangle$, and $\langle f_6 \rangle$). $\langle f_3 \rangle$, $\langle f_2 \rangle$, and $\langle f_5 \rangle$ of the CTA sample employed here were determined using $\langle F \rangle$ ($= 2.92$), as 0.92, 1.01, and 0.99, respectively. These values are approximately the same as those (0.89, 1.02, 1.00) evaluated by Kamide and Okajima⁹ for similar CTA sample.

The peak at the highest magnetic field ($\delta = 2.03$ ppm) pyridine is extremely sharp, compared with the other two peaks. This suggests that the peak at $\gamma = 2.03$ ppm has a long spin-spin relaxation time T_2 and may be due to low molecular weight compounds contaminated in the solution. The peak intensity at $\delta = 2.15$ ppm is almost twice that at $\delta = 2.04$ ppm and we may assign the peak at $\delta = 2.15$ ppm to the *O*-acetyl methyl proton at C_2 and C_6 positions (AMH_2 and AMH_6) and the peak at $\delta = 2.04$ ppm to the *O*-acetyl methyl proton at C_3 position (AMH_3). The intensity ratios of three peaks, observed in TCM, acetone, and DMSO over the range of 1.6–2.4 ppm, were almost independent of the solvents. The peaks from higher magnetic field can be attributed to the *O*-acetyl methyl protons at C_3 , C_2 , and C_6 positions. An exception is DMAc, in which the peak intensity at $\delta = 1.97$ ppm (probably assigned for AMH_2) is about 10–15% smaller than other two peak intensities, suggesting a small probability of resonance absorption by AMH_2 at 1.94 and 2.07 ppm, in addition to at 1.97 ppm. Here, we analyzed the spectrum in DMAc on the assumption that each peak attributes to the *O*-acetyl methyl proton at C_3 , C_2 , and C_6 positions (from higher magnetic field), respectively.

Table I shows the chemical shifts of the *O*-acetyl methyl protons of CTA in various solvents. Figure 2 shows the ^{13}C NMR spectra of the *O*-acetyl carbonyl carbon region of CTA. Until very recently, the peak assignment of the carbonyl carbon region in ^{13}C NMR spectra was an unsolved problem. Applying a low-

Table I. NMR chemical shift of *O*-acetyl methyl proton and carbonyl carbon in cellulose triacetate solution at 40°C

Solvent	Chemical shift ^a					
	<i>O</i> -Acetyl methyl proton			<i>O</i> -Acetyl carbonyl carbon		
	C ₆ ^b	C ₂	C ₃	C ₆	C ₂	C ₃
DMAc ^c -d ₉	2.07	1.97	1.94	—	—	—
DMSO ^d -d ₆	2.06	1.94	1.88	169.9	169.0	168.7
acetone-d ₆	2.08 ^e	1.96 ^e	1.92 ^e	170.7	169.9	169.5
pyridine-d ₅	2.15	2.15	2.04	170.5	169.9	169.5
TCM ^f -d ₁	2.12	2.00	1.95	170.0	169.5	169.1

^a 0 ppm for tetramethylsilane.^b Carbon position substituted by *O*-acetyl methyl group.^c *N,N*-Dimethylacetamide.^d *N,N*-Dimethylsulfoxide.^e Measured by water eliminated Fourier transform method.^f Trichloromethane. **Figure 2.** ¹³C NMR spectra of cellulose triacetate ($\langle F \rangle = 2.92$) in various deuterated solvents in *O*-acetyl carbonyl carbon region. a) DMSO-d₆; b) acetone-d₆; c) pyridine-d₅; d) TCM-d₁.

power selective decoupling method to acetyl methyl proton located at specific carbon position, Kowsaka *et al.*¹² made the most reason-

able assignments. Three large peaks were assigned to the acetyl groups at C₆, C₃, and C₂ positions, from the low magnetic field side.

Table II summarizes T_1 of the *O*-acetyl methyl proton and *O*-acetyl carbonyl carbon in various solvents. Here, T_1 for *O*-acetyl methyl proton at C₆ in TCM and DMSO and for *O*-acetyl methyl proton at C₂ in pyridine system could not be determined because of the overlapping of the peaks due to impurities in these solutions. T_1 of the *O*-acetyl methyl proton at C₃ position decreases in the following order; acetone > DMSO = TCM ≥ pyridine. No significant solvent dependence of T_1 of the *O*-acetyl methyl proton at C₂ position was detected experimentally. T_1 of the carbonyl carbon at C_i ($i=2, 3, 6$) position varies depending on the carbon positions, to which the *O*-acetyl group is attached. T_1 of the carbonyl carbon at C₆ position attains a maximum in acetone and minimum in DMSO. For the carbonyl carbon at C₂, T_1 decreases in the following order: acetone ≫ TCM > pyridine > DMSO and for the carbonyl carbon at C₃, acetone ≫ DMSO > TCM > pyridine. It is generally considered that ¹³C nucleus relaxation is attributable most to the relaxation due to

Table II. Spin-lattice relaxation time (T_1) of the *O*-acetyl methyl proton and *O*-acetyl carbonyl carbon in cellulose triacetate solution

Solvent	T_1/s					
	<i>O</i> -Acetyl methyl proton			<i>O</i> -Acetyl carbonyl carbon		
	C ₆ ^a	C ₃	C ₂	C ₆	C ₃	C ₂
DMSO ^b - <i>d</i> ₆	— ^c	0.80	0.77	2.25	2.33	2.41
pyridine- <i>d</i> ₅	0.77 ^d	0.77 ^d	— ^c	2.56	2.26	2.46
TCM ^e - <i>d</i> ₁	— ^c	0.80	0.77	2.83	2.28	2.49
acetone- <i>d</i> ₆	— ^f	0.85	0.77	3.27	3.36	2.61

^a Carbon position substituted by *O*-acetyl group.^b *N,N*-Dimethylsulfoxide.^c Overlapping with the peak of impurity.^d Overlapping with neighboring CTA peaks.^e Trichloromethane.^f Overlapping with solvent peak.

dipole-dipole interaction between ^{13}C nucleus and ^1H nucleus (its relaxation time hereafter referred to as T_1^{DD}). In the case of CTA, there is no ^1H nucleus directly combined with the *O*-acetyl carbonyl carbon and a possible interaction of the carbonyl carbon with ^1H nucleus attached to glucopyranose ring (skeleton) carbon and ^1H nucleus in the *O*-acetyl methyl group may be negligible because a reciprocal of T_1^{DD} decreases rapidly in reverse proportion to the sixth power of the distance of ^{13}C and ^1H nuclei. Therefore, we can conclude that the difference in T_1 of the carbonyl carbon reflects a difference of the interaction between the *O*-acetyl group and the solvent: shorter T_1 for stronger interaction. T_1 was the longest in acetone for all carbon positions. This means that the interaction of acetone molecule with the *O*-acetyl carbonyl carbon is the weakest among the four solvents examined, regardless of the carbon position. T_1 of the carbonyl carbons at three positions decreases in the following order in each solvent: in DMSO $\text{C}_2 > \text{C}_3 > \text{C}_6$; in pyridine $\text{C}_6 > \text{C}_2 > \text{C}_3$; in TCM $\text{C}_6 > \text{C}_2 > \text{C}_3$; in acetone $\text{C}_3 \geq \text{C}_6 > \text{C}_2$.

Figures 3 and 4 show schematic representation of the NMR spectra of the *O*-acetyl

methyl proton and the *O*-acetyl carbonyl carbon of the CTA in five solvents. The number in the figures means the difference (ppm) from δ in acetone. When acetone is taken as the standard, the peaks of the methyl protons at three carbon positions are shifted downfield in pyridine and TCM and to upfield in DMSO. In DMAc the proton peak at C_6 position slightly shifts upfield, but the proton peaks at C_2 and C_3 positions downfield. On the other hand, all the peaks of the carbonyl carbons, except for those at C_2 and C_3 positions in pyridine, shift more than 0.2 ppm upfield.

Based on the above experimental results, we can consider that in CTA-solvent systems, there exist some interactions between the *O*-acetyl group and the solvent molecules.

(1) TCM and Pyridine

The chlorine atom in TCM molecule has a strong electron donating property to act with *O*-acetyl carbonyl carbons located at C_2 , C_3 , and C_6 (Figure 4c), resulting in shielding of the *O*-acetyl carbonyl carbons, whose ^{13}C NMR peaks shift to a higher magnetic field than those of the carbonyl carbon of acetone. For this reason, weakening of the double bond nature of the carbonyl group brings about

Figure 3. ^1H -NMR chemical shift δ (in ppm) of *O*-acetyl methyl proton of CTA molecules in various deuterated solvents. Number of each bar denotes the difference of the δ value between that in acetone and in other solvents.

Figure 4. ^{13}C NMR chemical shift δ (in ppm) of *O*-acetyl carbonyl carbon of CTA molecules in various deuterated solvents. Number of each bar denotes the difference of the δ value between that in acetone and in other solvents.

Figure 5. Schematic representation of the interaction between a CTA molecule and various solvents.

deshielding of the *O*-acetyl methyl carbon, shielding before and a downfield shift of the *O*-acetyl methyl proton peak. Figure 5a shows a schematic representation of the interaction be-

tween the CTA molecule and the TCM molecules. Tertiary amine in pyridine also acts as an electron donor and seems, judging from Figure 4b, to interact only with the *O*-acetyl

carbonyl carbon at C₆ position as demonstrated in Figure 5b. Unfortunately, it is not understood why the large shift of δ of *O*-acetyl methyl protons at C₂ and C₃ positions toward lower magnetic field side occurs and why the tertiary amine has an interaction only to *O*-acetyl carbonyl carbon at C₆ position.

(2) DMSO

The oxygen atom in the DMSO molecule donates electrons to *O*-acetyl carbonyl carbons at C₂, C₃, and C₆ positions, resulting in a significant shift of the acetyl carbonyl carbon peak to upfield. This also brings about weakening of the shielding effect, originally existing between the *O*-acetyl carbonyl carbon and carbonyl oxygen. As a result, the peaks of *O*-acetyl methyl protons are expected to shift to a lower magnetic field. However, the experimental data show the shift of the peaks to a higher magnetic field, suggesting electrostatic interaction between the oxygen atom in DMSO and *O*-acetyl methyl protons. Figure 5c illustrates the solvent effect of DMSO on the CTA molecule. Note that, although DMSO has a similar chemical structure to acetone, the former strongly interacts with the *O*-acetyl group as compared with the latter. This conclusion was deduced from the chemical shifts of *O*-acetyl methyl proton and carbonyl carbon and from T_1 of the *O*-acetyl carbonyl carbon, and is quite consistent with the higher polarity of sulfonyl group than that of the carbonyl group.

(3) DMAc

Figure 3a shows that an interaction between *O*-acetyl group at C₆ position and DMAc is

expected to be small and that there occurs an interaction between *O*-acetyl group at C₂ and C₃ and DMAc and the interaction at C₃ position may be a little stronger than that at C₂ position. This can be explained by the amphoteric nature of the DMAc molecule. Figure 5d schematically illustrates the interaction of DMAc with the CTA molecule.

Summarizing, it can be concluded that the solvent molecule interacts significantly with the *O*-acetyl groups of cellulose triacetate and that the extent of solvation varies depending on the positions at which the *O*-acetyl group is located and on the solvent nature.

REFERENCES

1. See, for example, W. R. Moore, and R. M. Tidwell, *Makromol. Chem.*, **81**, 1 (1965); W. R. Moore, *J. Polym. Sci., C*, **No. 16**, 571 (1967); W. R. Moore, International Symposium on Solution Properties of Natural Polymers, Edinburgh, 1967.
2. K. Kamide and M. Saito, *Eur. Polym. J.*, **20**, 903 (1984).
3. K. Kamide, K. Okajima, and M. Saito, *Polym. J.*, **13**, 115 (1981).
4. K. Kamide, T. Terakawa, and Y. Miyazaki, *Polym. J.*, **11**, 285 (1979).
5. K. Kamide, Y. Miyazaki, and T. Abe, *Polym. J.*, **11**, 523 (1979).
6. K. Kamide, M. Saito, and T. Abe, *Polym. J.*, **13**, 421 (1981).
7. M. Saito, *Polym. J.*, **15**, 249 (1983).
8. K. Kamide and M. Saito, *Polym. J.*, **14**, 517 (1982).
9. K. Kamide and K. Okajima, *Polym. J.*, **13**, 127 (1981).
10. V. W. Goodlett, T. J. Dougherty, and H. W. Patton, *J. Polym. Sci., A-1*, **9**, 155 (1971).
11. N. Shiraishi, T. Katayama, and Y. Yokota, *Cellulose Chem. Tech.*, **12**, 429 (1978).
12. K. Kowsaka, K. Okajima, and K. Kamide, *Polym. J.*, **18**, 843 (1986).