Solid-State ^{13}C NMR Study of Na−Cellulose Complexes

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The interaction of microcrystalline cellulose from cotton and aqueous sodium hydroxide was investigated by ^{13}C NMR solid-state spectroscopy as a function of temperature and sodium hydroxide concentration. When the concentration of NaOH was increased, the initial cellulose spectrum was replaced successively by that of Na−cellulose I followed by that of Na−cellulose II. In Na−cellulose I, each carbon atom occurred as a singlet, thus implying that one glucosyl moiety was the independent magnetic residue in the structure of this allomorph. In addition, the occurrence of the C6 near 62 ppm is an indication of a *gt* conformation for the hydroxymethyl group of Na−cellulose I. In Na−cellulose II, the analysis of the resonances of C1 and C6 points toward a structure based on a cellotriosyl moiety as the independent magnetic residue, in agreement with the established X-ray analysis that has shown that for this allomorph, the fiber repeat was also that of a cellotriosyl residue. For Na−cellulose II, the occurrence of the C6 in the 60 ppm region indicates an overall *gg* conformation for the hydroxymethyl groups. A comparison of the spectra recorded at 268 K and at room temperature confirms the stronger interaction of NaOH with cellulose when the temperature is lowered. In the Q region, corresponding to NaOH concentrations of around 9% and temperatures below 277 K, most of the sample was dissolved and no specific solid-state ^{13}C NMR spectrum could be recorded, except for that of a small fraction of undissolved cellulose I. The same experiment run on a wood pulp sample leads to a new spectrum, with spectral characteristics different from those of Na−cellulose I and Na−cellulose II. This new spectrum is assigned to the Q phase, which appears to result from topological constraints that are present in whole wood pulp fibers but not in microcrystalline cellulose. A spectrum recorded for samples in the Na−cellulose III conditions resembled that of Na−cellulose II but of lower resolution. Similarly, a spectrum of a sample of Na−cellulose IV was identical to that of hydrated cellulose II. These observations have allowed us to propose a simplified phase diagram of the cellulose/NaOH system in terms of temperature and NaOH concentration. This diagram, which is simpler than the one deduced from X-ray analysis, consists of only four different regions partially overlapping.

Introduction

It is now more than 150 years since that John Mercer has shown that native cellulose fibers could be readily modified by a treatment with alkali solutions.[1] This modification—the so-called "mercerization" process—which is still being used commercially today yields fibers with enhanced mechanical properties and superior dyeability. Following the pioneering work of Mercer, the use of sodium hydroxide as well as other alkalis on cellulose has been broadly extended and has turned to be one of the major "activation" steps leading to the preparation of numerous commercial cellulosics. The alkalization of cellulose is indeed a prerequisite to the preparation of many cellulose derivatives, the spinning of viscose, or the manufacturing of cellulose-based sponges, etc. The development of these products has required a large number of basic and applied studies, where the fundamental aspects of the interaction of cellulose with aqueous sodium hydroxide and alkali solutions in general have been investigated. A number of reviews and book chapters summarize the results of these studies.[2−5]

In its interaction with cellulose, aqueous sodium hydroxide above a certain concentration is able to penetrate the cellulose crystalline lattice to yield a series of more or less well-defined crystalline complexes holding a number of sodium ions and water molecules within their crystalline lattice. The analysis of these complexes by X-ray diffraction analysis has been attempted by a number of authors.[6−14] It is generally accepted that the immersion of ramie or cotton fibers into 12−16% (w/v) NaOH yields Na−cellulose I, whereas the use of more concentrated alkali, typically 32% (w/v) NaOH, gives another allomorph: Na−cellulose II. Whereas Na−cellulose I is unique, Na−cellulose II occurs under two forms, the colorless IIA and the bright blue IIB, depending on whether the fibers were constrained or not during the transformation.[9] The conversion of Na−cellulose I into Na−cellulose III is obtained by vacuum drying Na−cellulose I, whereas washing sodium−cellulose I and Na−cellulose II until neutrality, yields the sodium-free Na−cellulose IV, which in its turn will give cellulose II upon drying. Another allomorph, namely, Na−cellulose V, has also been reported, but its existence as a true identity has been controversial.[14−16] The survey of the X-ray fiber diagram of the various cellulose allomorphs indicates that, whereas most allomorphs maintain the classical cellobiosyl repeat of cellulose I and cellulose II, Na−cellulose II takes a fiber repeat of 1.54 nm, indicating a cellotriosyl repeat.[9,13] Thus in this last

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allomorph, the insertion of Na^+ into the crystalline lattice leads to a drastic modification of the conformation of the cellulose molecule backbone that adopts a 3-fold periodicity as opposed to the classical 2-fold one.

In two seminal papers, Sobue et al. and Sobue[15,16] have presented a phase diagram of ramie cellulose and its various Na−cellulose crystalline complexes as a function of temperature and concentration of sodium hydroxide. This diagram, established between −20 and 100 °C, indicates the zones of occurrence of the various Na−celluloses. Quite unexpectedly, it revealed a new highly swollen and poorly crystalline allomorph, namely, Na−cellulose Q, occurring at NaOH concentrations between 7% and 8% and temperatures between −5 and 1 °C. More recently, it was found that a systematic exploration of this region of the diagram could lead to a total dissolution of cellulose if an adequate pretreatment was applied to the starting cellulose.[17−19] Typical solutions of 5% cellulose could be obtained at a sodium hydroxide concentration of 9% and temperature of 4 °C and below. Such solutions are being tested for the spinning of cellulose,[20−22] creating cellulose-based food products,[23] reprocessing sausage casing,[24] or preparing cellulose-based cellular composites.[25]

The crystal structure determination of Na−cellulose complexes from X-ray fiber diffraction analysis alone has proven difficult since the corresponding X-ray patterns are far less resolved than those of the uncomplexed cellulose allomorphs. In addition, the interpretation of the patterns are sometimes complicated by the coexistence of several allomorphs in a given sample. An attempt of structure determination of Na−cellulose I has been made by Nishimura et al.,[11] who have tentatively proposed a four-chain unit cell organized in the $P2_1$ space group. Such complexity is, however, contradicted by the simplicity of the ^{13}C solid-state NMR spectrum of this Na−cellulose where each cellulose carbon atom seems to occur as a singlet.[26−28] Thus, it appears that for this Na−cellulose complex, the analysis of the X-ray data alone is not sufficient to give a clear picture of the interaction of the Na^+ ions with the cellulose molecules. A thorough analysis of ^{13}C solid-state NMR data, which has been critical for the progress of the crystallography of cellulose,[29] should therefore be also applied to the description of the various Na−cellulose complexes. In fact, ^{13}C solid-state NMR spectra of Na−cellulose complexes have already been reported, and their analysis has shown some evidence of the structural modifications that take place when cellulose interacts with alkali solutions.[26−28,30−33] In most of these earlier works, however, the low spectral resolution did not lead to a clear assignment of the resonances belonging to the various complexes, and it seems that more knowledge could be deduced from ^{13}C solid-state NMR data if better instrumental conditions could be used. In the present study, we have attempted to gain this further knowledge by using microcrystalline cellulose from cotton linters as a starting material, subjecting them to alkalization at different temperatures and concentration, and recording their ^{13}C solid-state NMR spectra with improved spectral resolution. The analysis of these spectra allows us to present an improved NMR-based phase diagram of cellulose complexed with NaOH as a function of alkali concentration and temperature. This diagram presents at the same time some similarity and difference from the earlier X-ray-based diagram of Sobue et al.[15]

Experimental Section

Materials. Cotton linters from Tubize and LV dissolving wood pulp from Borregaard were kindly supplied by Spontex. HCl 35% and sodium hydroxide, both of analytical grade, were purchased from SDS.

Sample Preparation. *Microcrystalline Cellulose.* Microcrystalline cellulose was prepared by boiling cotton linters under reflux in 3 N HCl for 2 h. The resulting hydrolyzed samples were centrifuged, and the pellets were redispersed in distilled water followed by washing with successive centrifugation until neutrality. The final pellet was redispersed in distilled water and freeze-dried.

Alkali Cellulose. The samples of microcrystalline cellulose were dispersed in aqueous sodium hydroxide of concentrations ranging from 8% to 50% (w/v). Regarding the concentration of cellulose with respect to the aqueous NaOH, it was found that a too high concentration did not allow the full conversion into Na−cellulose. For this reason, all experiments were achieved with a solid concentration of 12% (w/w) which was found to be the highest where all native cellulose was amenable to the conversion into Na−cellulose. After stirring the mixtures for 1 h, a white gel was obtained, which was kept at rest for 24 h at the chosen temperature for subsequent NMR analysis.

NMR Measurements. ^{13}C CP/MAS (cross-polarization magic-angle spinning) NMR spectra of Na−cellulose samples were measured with a Bruker MSL spectrometer operating at 50 MHz for ^{13}C and equipped with a variable temperature unit. ^{13}C and ^{1}H field strengths of 64 kHz, corresponding to a 90° pulse width of 4 μs, were used for the matched spin-lock cross-polarization transfer. The magic-angle spinning frequency was set at about 2000 Hz. The contact time was 1 ms, the acquisition time was 70 ms, the sweep width was 29 400 Hz, and the repetition time was 4 s. For SP/MAS (single-pulse magic-angle spinning) experiments, the ^{13}C 90° pulse width was 3.5 μs, while all other acquisition parameters were left the same as for the CP/MAS experiments. A 4 s repetition time allowed the detection of dissolved cellulose. Chemical shifts relative to tetramethylsilane were measured after external calibration with the carbonyl signal of glycine at 176.03 ppm. A typical number of 20 000 scans were acquired for each spectrum. Na−cellulose mixtures were inserted into 7 mm o.d. zirconia rotors and sealed with Kel-F caps. The temperature of the NMR experiments was kept at the same temperature as that of the sample preparation. As the temperature is critical for the preparation and stability of the various Na−cellulose allomorphs, special care was taken to avoid any change in temperature between a sample preparation and the recording of its spectrum. The deconvolution was performed by assigning Lorentzian line shapes to crystalline resonances, whereas Gaussian line shapes were used for the disordered contributions.

Results and Discussion

CP/MAS Experiments at Room Temperature. Typical solid-state spectra of mixtures of microcrystalline cellulose with aqueous NaOH, of increasing concentration, recorded at 293 K are shown in Figure 1, whereas the values of the chemical shifts of the carbon atoms C1, C4, and C6 are listed in Table 1, and their variation is schematically represented in Figure 2. Below 13% NaOH, the initial cellulose spectrum remains unmodified (Figure 1A), but starting at 13%, new resonances are observed in the C1, C4, and C6 ranges, indicating a first transition (Figure 1B). These new resonances are shifted by about 2 ppm with respect to the corresponding ones in the initial cellulose: downfield for the signal assigned to C1 and upfield for those corresponding to C4 and C6. When the soda concentration is of 18%, all features from the initial cellulose have disappeared and only the new signals that started to appear in the 13% spectrum are present, yielding a fairly sharp five-singlet spectrum (Figure 1C). When the concentration of soda reaches 25%, a second transition starts to occur, indicated by the onset

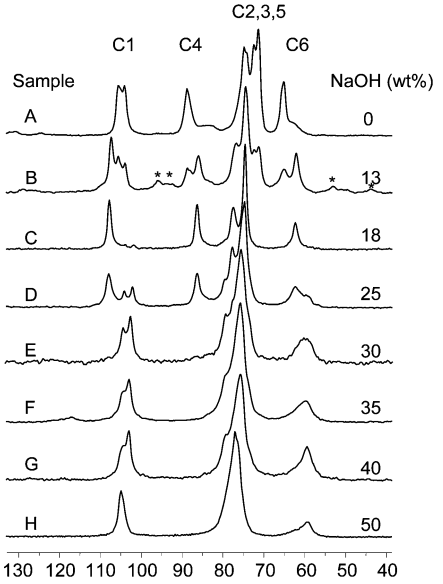

Figure 1. ^{13}C CP/MAS NMR spectra of microcrystalline cellulose from cotton immersed into aqueous NaOH solutions at room temperature. (A) Initial sample. (B) Immersed into 13% NaOH. The asterisks correspond to spinning bands. (C) As in (B), but into 18% NaOH. (D) Into 25% NaOH. (E) Into 30% NaOH. (F) Into 35% NaOH. (G) Into 40% NaOH. (H) Into 50% NaOH.

Table 1. Chemical Shifts of C1, C4, and C6 for Cellulose I, Sodium−Cellulose I, Sodium−Cellulose II, Sodium−Cellulose Q, and Dissolved Cellulose

	chemical shifts (ppm)		
	C1	C4	C6
cellulose I	105.6 104.1	88.6 83.7	65.0 62.9
Na−cellulose I	107.1	85.3	62.1
Na−cellulose II	104.3 102.4	79.5	61.1, 60.3, 59.5
Na−cellulose Q	106.9 104.2	85.5 83.0	61.3
dissolved cellulose	104.2	79.4	60.9

of an upfield doublet in the C1 region and a new broad upfield peak in the C6 region (Figure 1D). This second transition is complete when the soda concentration reaches 30% (Figure 1E). In this spectrum, the doublet in the C1 region consists of a strong resonance at 102.4 ppm and a weaker one at 104.3 ppm. In Figure 1, spectrum 1E, the C6 resonance, which is rather broad, is indicative of a multiplet. Its center is shifted upfield near 60.3 ppm, i.e., by nearly 2 ppm with respect to Figure 1, spectrum 1C, and close to 5 ppm with respect to Figure 1, spectrum 1A. Another feature of Figure 1, spectrum 1E, is that the C4 resonance is located at 79.5 ppm and therefore is also shifted upfield by more than 8 ppm with respect to its position in the initial cellulose sample. When the soda concentration is further increased from 30% to 50% no clear transition is observed, but the spectra become less resolved and there is a merging of the resonances that leads to a simplified spectrum consisting of only three broad bands (Figure 1H). With increasing NaOH content, the two resonances at C1 merge around 105 ppm (Figure 2A), whereas the C4 peak becomes broader to the point where it merges with the group of resonances of C2, C3, C5 near 79 ppm (Figure 2B). As shown in Figure 1, the resonance at C6, which initially consists of a sharp peak near 65 ppm and a shoulder near 62.9 ppm, yields a single peak centered at 62.1 ppm at 18% NaOH. This peak is again shifted upfield near 60.4 ppm when going from 30% to 50% NaOH, and there is a narrowing of the peak during such increase in NaOH concentration.

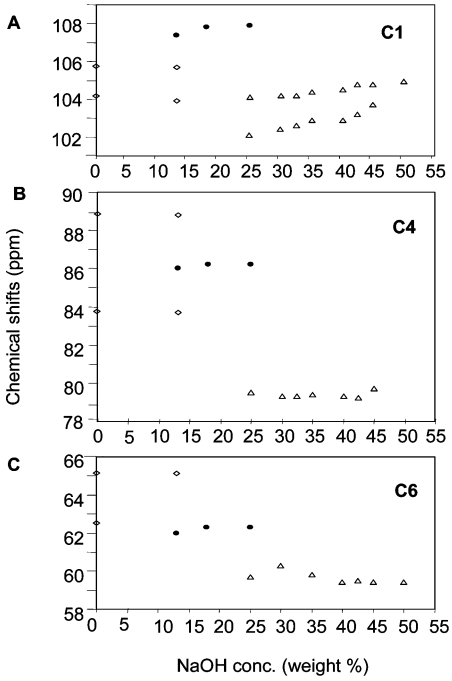

Figure 2. Variation of the chemical shifts in the ^{13}C CP/MAS NMR spectra of microcrystalline cellulose from cotton immersed in NaOH solutions as a function of the alkali concentration. Upper panel: variation of the C1. Middle panel: variation of the C4. Bottom panel: variation of the C6. Open diamond, native cellulose; filled circles, Na−cellulose I; open triangles, Na−cellulose II.

The spectra shown in Figure 1 can be correlated with those already published. In agreement with literature data, Figure 1, spectrum 1C, corresponds to Na−cellulose I.[26−28] In this allomorph, each carbon atom gives rise only to a singlet, so a single glucosyl moiety of cellulose appears to be the magnetically independent residue of the structure. This observation contradicts the structural determination made by Nishimura et al.[11] who have proposed a crystalline structure for Na−cellulose I. Their model is based on four independent cellulose chains, and there are eight crystallographically independent glucosyl residues in the structure. This plurality should lead to multiplets for at least one or some of the carbon resonances, but this is not the case, neither in our spectrum, nor in those already in literature. A further discrepancy between the X-ray data proposed by Nishimura et al.[11] and the present ^{13}C solid-state NMR data deals with the conformation of the hydroxymethyl groups of Na−cellulose I. Indeed, in the structure of Nishimura et al.,[11] half of the cellulose hydroxymethyl groups have the *tg* conformation, whereas those of the other half are in the *gt* situation. In keeping with the well-established relation defined by Horii et al., that correlates the chemical shift of C6 in cellulosics with that of the hydroxymethyl group conformation,[34] this structure should yield two regions for the ^{13}C NMR resonances of the C6 position: one near 65 ppm, corresponding to glucosyl moieties having the *tg* conformation, and one near 62 ppm assigned to those in *gt* situation. This is not the case, since in the spectrum of Na−cellulose I (Figure 1C), there is only one region for the resonance of C6. Its position near 62 ppm clearly indicates an exclusive *gt* conformation for this allomorph. This observation is one more argument in favor of a revision of the Nishimura et al.[11] structure of Na−cellulose I.

The spectrum in Figure 1E, which is that of Na−cellulose II, is better resolved than any we were able to find in the literature.[35,36] Here, the multiplets at C1 and C6 point toward

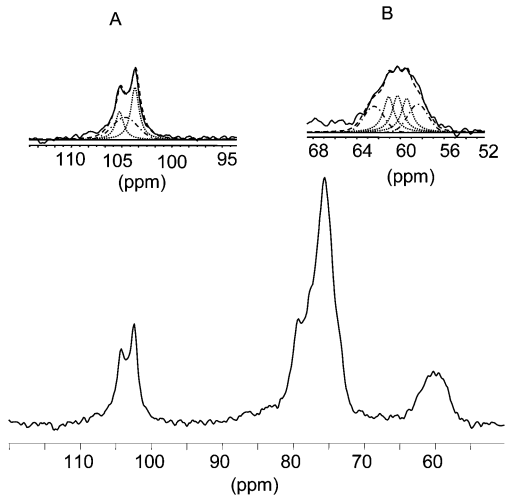

Figure 3. Same as Figure 1E. Insets: deconvolution of the C1 and C6 regions of the spectrum.

the presence of three magnetically independent glucosyl moieties for the cellulose chains in this complex. The deconvolution of the C1doublet (Figure 3A) yields an upfield resonance that is twice as strong as its downfield counterpart. The C6 resonance is a clear triplet, which after deconvolution yields the three resonances of equal intensity (Figure 3B), centered at 59.5, 60.3, and 61.1 ppm. At first glance, this observation seems to be well correlated with the X-ray data recorded on crystalline Na−cellulose II, which indicate that this allomorph bears a repeat distance of 1.54 nm corresponding to a cellotriosyl repeat.[9] Despite this periodicity, a model made by Whitaker et al.,[13] based on the refinement of X-ray fiber data, has defined the crystalline structure of Na−cellulose as consisting of two equivalent cellulose chains, each organized along a 3-fold screw axis parallel to the fiber direction.[13] Such high symmetry should imply that it is one glucosyl and not a cellotriosyl residue that is the crystallographic repeat unit. Transposed into ^{13}C solid-state NMR data, each carbon signal should therefore occur as a singlet. As seen in Figure 1E and Figure 3, parts A and B, this is clearly not the case, and thus, the structure of Na−cellulose II must be somewhat more complex than the one defined by the simple set of coordinates listed by Whitaker et al.[13] The observation of three magnetically independent glucosyl moieties in Na−cellulose II and their assignment to a cellotriosyl residue with three sets of conformation is therefore the simplest possibility. Other models, consisting of more chains and larger unit cells, could be envisaged from our NMR data alone, but they would be difficult to reconcile with the established crystalline unit cell of Na−cellulose II.[9,13] Besides these discrepancies, Whitaker et al.[13] indicate that the hydroxymethyl group of their Na−cellulose II model is in the *gg* conformation. This situation is in agreement with the occurrence of the C6 resonances at 59.5, 60.3, and 61.1 ppm in our spectrum: these values are indeed in the *gg* conformational region, defined by Horii et al.[34] for the cellulose allomorphs.

Another feature of the Na−cellulose II spectrum is that of the C4 resonance, which is dramatically shifted upfield by more than 8 ppm with respect to its position in the initial cellulose sample. In Na−cellulose II, the resonance of C4 goes very close to 80 ppm, which is the region where this carbon occurs in the spectrum of cellulose in NaOH solution.[17,37] As explained by Kamide et al.,[17] the large upfield shift of C4 and its merging with the resonances of C2, C3, and C5 in Na−cellulose II may be correlated with the breakage of the O3···O′5 hydrogen bond that stabilizes the glucosic linkage in crystalline cellulose. In

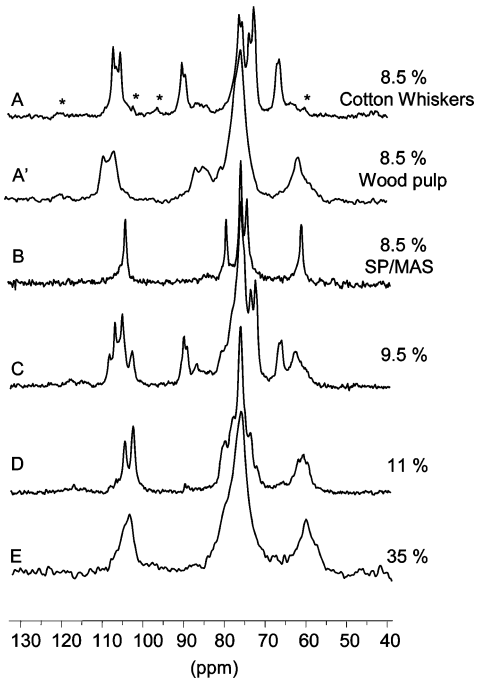

Figure 4. ^{13}C CP/MAS NMR spectra of microcrystalline cellulose from cotton and wood pulp immersed into aqueous NaOH solutions at 268 K. The asterisks correspond to spinning bands. (A) Microcrystalline cellulose from cotton into 8.5% NaOH. (A′) Wood pulp into 8.5% NaOH. (B) Same as (A), but in SP/MAS mode. (C) Same as A, but into 9.5% NaOH. (D) Same as (A), but into 11% NaOH. (E) Same as (A), but into 35% NaOH.

fact such breakage, resulting from the interaction of Na^+ ions with O3, O′5, and O′6, has been observed in the crystals of α-cellobiose·2NaI·2H_2O complex.[38] The extrapolation of this dimeric structure to cellulose points toward a left-handed cellulose structure with 2.9 residues per turn, i.e., very close to the proposed 3-fold crystalline structure of Na−cellulose II.[38] Remarkably, in xylan hydrate, which has a 3-fold crystalline structure homologous to that of Na−cellulose II,[13,39] and where there is no C3···O′5 hydrogen bond, one observes also a merging of the resonance of C4 with those of C2 and C3, as in Na−cellulose II.[40] Thus, this rule appears to be verified at least for the β1→4 glucans and β1→4 xylan.

CP/MAS Experiments at 268 K. The spectra recorded at 268 K are presented in Figure 4. At this temperature, the sample obtained from the microcrystalline cellulose dispersion corresponding to 8.5% NaOH has the appearance of a low viscosity and transparent solution, without any trace of fibrous structure observable by optical microscopy. The ^{13}C CP/MAS spectrum of this sample (Figure 4A) only reveals the presence of a small amount of undissolved native cellulose, whereas a ^{13}C SP/MAS spectrum of the same sample (Figure 4B) confirms that most of it consists of dissolved cellulose. Interestingly, a preparation made with only 4% w/w cellulose exhibits exactly the same cellulose I features (spectrum not shown). This clearly indicates that the remaining small amount of undissolved cellulose is not due to solubility limits. Moreover, this undissolved cellulose is obviously more crystalline than the original native cellulose, indicating that this difference in the solubilization maybe related to different crystallite sizes within the sample.

On the contrary to what was observed with microcrystalline cellulose from cotton, the spectrum obtained in the same conditions with wood pulp (Figure 4A′) exhibits spectral features not observed in the spectra obtained at room temperature. The

C1 and C4 resonances exhibit clear doublets at (106.9, 104.2) ppm and (85.5, 83.0) ppm, respectively, whereas the C6 carbon resonates at an apparent single position at 61.3 ppm. One part of the spectrum can be considered as a subset of the Na−cellulose I spectrum. This is confirmed by the increasing strength of the resonances at 106.9 and 85.3 ppm when the preparation is kept at room temperature for 1 day (spectrum not shown). The other part of the spectrum cannot be assigned to any other identified allomorph. This probably highly swollen cellulose structure which occurs only in presence of topological constraints, can thus be considered as the true Na−cellulose Q identified by Sobue et al. on swollen ramie fibers.[15,16] It is also worthy to note that such dramatic differences between microcrystalline cellulose from cotton and wood pulp fibers only occur in this limited part of the phase diagram. In the other parts, the spectra of these two cellulose samples are highly similar.

The spectrum corresponding to 9.5% NaOH (Figure 4C) presents a number of multiplets: typically four resonances for the C1, three for the C4 and three for the C6. When comparing this spectrum with those obtained at room temperature (Figure 1), one sees that it consists of the superposition of three subspectra : one spectrum corresponding to native cellulose, as in Figure 1A, one of Na−cellulose I as in Figure 1C, and one of Na−cellulose II as in Figure 1E. The spectrum corresponding to 11% NaOH (Figure 4D) is clearly that of pure Na−cellulose II, similar to Figure 1, spectrum 1E, but better resolved. In the same manner as the 30% NaOH room-temperature spectrum, the C1 and C6 resonances were also deconvoluted and confirmed the presence of three magnetically independent glucosyl moieties in Na−cellulose II. The sequence of spectra acquired at low temperature, with increasing NaOH concentration, resembles the sequence of those observed at room temperature. At high NaOH content, Figure 4, spectrum 4E, corresponding to the addition of 35% NaOH, showed the same merging of C1 resonances as in Figure 1, spectrum 1G, and can therefore be defined as belonging to the Na−cellulose II allomorphs, but of a poorer definition.

A comparison of the interaction of cellulose with aqueous NaOH at room temperature and 268 K yields interesting differences that are well highlighted by ^{13}C CP/MAS spectra. The nearly total dissolution of the microcrystalline cotton into 8.5% NaOH at 268 K is in line with the general behavior of cellulose in the Q region, defined by Sobue et al.[15,16] in their papers describing the behavior of cellulose in aqueous NaOH as a function of temperature and alkali concentration. The property of this region has been well documented, not only for the extensive swelling of ramie[15,16] but also for the dissolution of steam-exploded pulp[17,18,20,21] and that of cellulose sausage skins[24] as well as for the manufacturing of cellulose-based cellular composites.[25] Despite these applications, the understanding of the molecular interaction of cellulose with NaOH under the Q conditions remains to be deciphered. On one hand, it seems clear that the Na^+ ions interact more strongly with cellulose at 268 K rather than at room temperature. On the other hand, it has been shown that in the 8−10% NaOH concentration, the number of water molecules solvating NaOH is larger at low temperature than at room temperature.[41] Thus, it is likely that it is the combination of these two effects that explains the extreme swelling observed in ramie cellulose in this part of the cellulose/NaOH phase diagram[15,16] or in our wood pulp samples. Unlike the intact fibers, which consist of a tight assembly of nearly endless microfibrils, our microcrystalline cellulose suspensions are made of highly dispersed short microcrystals. Each of these element is thus completely free to accept as much NaOH hydrates as possible and thus to swell at will without being prevented to do so by the tight winding of cellulose microfibrils within fiber cell walls. This difference explains why most of our microcrystalline cellulose sample became solubilized under condition where intact wood fibers were only highly swollen. In fact, when wood cellulose fibers are highly disrupted, e.g., by a steam explosion treatment[18] or strong homogenization,[19,24] they also become solubilized when the Q conditions are applied.

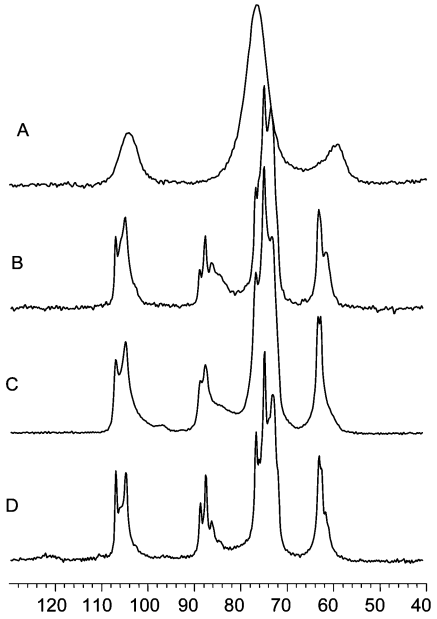

Figure 5. ^{13}C CP/MAS NMR spectra of microcrystalline cellulose from cotton immersed into aqueous 18% NaOH solutions at room temperature. (A) Na−cellulose III obtained after vacuum drying. (B) Same as in (A), but after washing with distilled water to produce Na−cellulose IV. (C) Same as in (B), but after vacuum drying. (D) Same as in (C), but after rehydration with distilled water.

Besides the very special case of the Q conditions, our low-temperature spectra can be well correlated with those of Kunze and Fink,[28] who have studied by ^{13}C NMR spectroscopy the effect of NaOH solution on dissolving pulp at room temperature and 248 K. From their experiments, these authors have showed that for the interaction of cellulose with NaOH, a decrease in temperature acted similarly to an increase in NaOH concentration. Our spectra show the same type of behavior with suspensions of cellulose microcrystals from cotton. With these, the enhanced influence of the Na^+ ions at low temperature is observed at all NaOH concentrations greater than 8.5%. This phenomenon is well illustrated by comparing the spectra in Figure 4 and those in Figure 1. For instance, a conversion into sodium−cellulose II is partial with 9.5% NaOH at 268 K (Figure 4C), but a concentration of 25% is required to achieve the same partial transformation at room temperature (Figure 1E). At 11% NaOH, the conversion into Na−cellulose II is total at 268 K, but it takes 30% NaOH to achieve the same transformation at room temperature.

^{13}C NMR Spectra of Na−Cellulose III and Na−Cellulose IV. The spectra of Na−cellulose III and Na−cellulose IV, together with those of cellulose II and rehydrated cellulose II, are shown in Figure 5. The spectrum of Na−cellulose III (Figure 5A), recorded on a sample resulting from vacuum drying of Na−cellulose I, does not show many features and appears to be identical to Figure 1, spectrum 1H, the cellulose sample that was immersed in 50% NaOH at room temperature and identified as Na−cellulose II. The sample of Na−cellulose IV (Figure

5B) resulting from the washing of Na−cellulose I presents more fine details, in particular in the C1, C4, and C6 regions. This spectrum resembles that of cellulose II (Figure 5C) and is quite indistinguishable from that of a rehydrated cellulose II sample (Figure 5D).

Whereas not much can be said about the spectrum of Na−cellulose III, which is poorly resolved, a correlation can be established between the spectrum of Na−cellulose IV and the X-ray structure of this allomorph proposed by Nishimura and Sarko.[12] The model proposed by these authors is based on two cellulose chains per unit cell, each chain being located on a 2-fold screw axis, but there is no symmetry relation between the two chains. Thus, in their model, there are two glucosyl moieties that are the crystallographically independent residues. In agreement with this observation, the ^{13}C NMR spectrum in Figure 5B displays a series of doublets for C1, C4, and C6, in the same manner as cellulose II, which is also based on two independent crystallographic glucosyl residues. Another factor of agreement between the structure of Nishimura and Sarko[12] and the present spectrum relies in the conformation of the hydroxymethyl moieties. Indeed in the refined X-ray structure of Na−cellulose IV presented by these authors, these groups have the *gt* conformation. In the present study, this conformation is confirmed by the value of the chemical shift of the C6 resonances at 63.4 and 61.8 ppm, both values being in the *gt* region defined by Horii et al.[34]

The great similarity between the spectra of the rehydrated cellulose II and that of Na−cellulose IV spectra suggests that this last allomorph corresponds to a cellulose II structure, with more or less disorder. This observation is in agreement with the crystallographic determination of Na−cellulose IV, which has also shown the great similarity existing between Na−cellulose IV and cellulose II.[12] Indeed, both crystalline structures contain two independent cellulose chains, each of them positioned along a 2_1 symmetry axis. In addition, in cellulose II as well as in Na−cellulose IV, the hydroxyl moieties of both cellulose chains have the *gt* conformation.

Cellulose NaOH Phase Diagram Deduced from ^{13}C NMR Spectroscopy. The NMR results presented in this study allow us to propose a phase diagram, based on the occurrence of Na−cellulose I and Na−cellulose II together with the Q region where cellulose is essentially soluble. This phase diagram, presented in Figure 6, define six regions, two of them being border zones where two phases are present at the same time. This diagram illustrates the increase in the swelling and dissolving power of aqueous NaOH toward cellulose at low temperature. A diagram such as the one in Figure 6 is simpler than the one of Sobue et al.,[15,16] deduced from X-ray analysis. Indeed, these authors have identified five Na−cellulose allomorphs presenting specific X-ray signatures, namely, Na−cellulose I, Na−cellulose II, Na−cellulose III, Na−cellulose V, and Na−cellulose Q. In the case of ^{13}C solid-state spectra, only two clear allomorphs are identified with specific NMR signature: Na−cellulose I and Na−cellulose II. The other allomorphs, Na−cellulose III and Na−cellulose V defined in the Sobue et al. diagram[15,16] give ^{13}C solid-state spectra that can be related to the pure or coexisting allomorphs Na−cellulose I and Na−cellulose II. In the case of Na−cellulose Q, a specific X-ray diagram can be obtained, but specific NMR signals were observed only in the case of wood pulp. For the suspensions of microcrystalline cellulose from cotton, we could observe essentially a cellulose solution together with some undissolved cellulose, still in the native cellulose form.

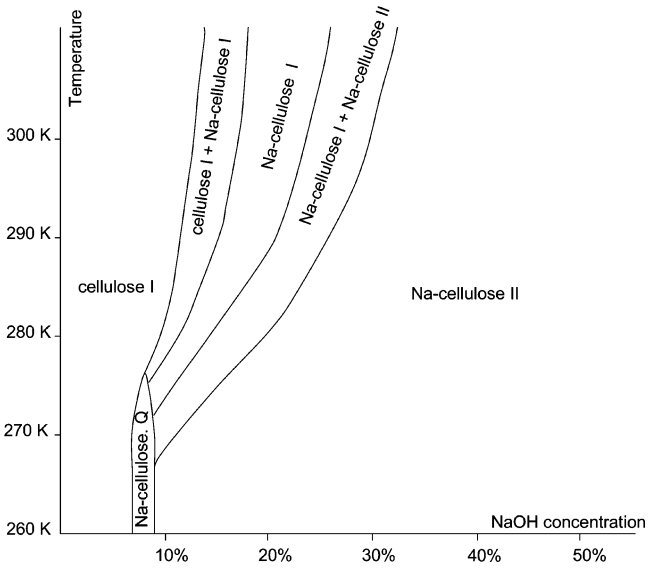

Figure 6. Na−cellulose phase diagram deduced from the ^{13}C CP/MAS NMR spectra of microcrystalline cellulose from cotton immersed into aqueous NaOH solutions.

As aforementioned, the narrow Q region of the diagram has been attracting a substantial interest in the last 15 years. Indeed, it is felt that the mastering of the dissolution of cellulose in aqueous NaOH alone should lead to a cheaper way to process cellulose materials from solution. At present, a number of cellulose products, such as yarns, films, cellular materials, etc., rely on the viscose process, which is slowly being phased out in a number of countries for environment problems. In the cellulose spinning process, a simple replacement of viscose by solutions of cellulose in aqueous NaOH should have the great advantage of using the current viscose wet-spinning lines and acid coagulation baths while avoiding the sulfur-related pollution. Despite this hope, the solutions of cellulose in aqueous NaOH have proven difficult to prepare and to stabilize. In the best cases, the solubility of cellulose in aqueous NaOH in the Q conditions is very low, typically only 5−6% for wood pulp.[21] Nevertheless, experimental cellulose filaments, having properties similar to those of viscose rayon, have been spun from such solutions.[22] Despite this achievement, the solubility of cellulose in aqueous NaOH is far too low to lead to a commercial operation. It is why a number of additives have been tested to increase the solubility of cellulose into aqueous NaOH at low temperature. In this line, one can quote an old report of Davidson,[42] who has shown that the addition of zinc and beryllium oxide improved somewhat the solubility of cellulose in the Q region. More recent reports have shown that the addition of urea,[28,43] thiourea,[44] or both components[45] to the NaOH solutions also improved somewhat the dissolution of cellulose at low temperature. With the use of such additives, it was possible to prepare stable cellulose NaOH solutions containing 7−8% of dissolving pulp. It remains to be seen whether such systems will be industrialized.

On a pure scientific ground, the solubilization of cellulose in the very narrow Q region of 8−9% NaOH and at temperatures of 4 °C and below is quite remarkable. Although at higher NaOH concentration, its seems that the Na^+ interacts directly with cellulose to form the insoluble Na−cellulose, at the Q concentration, this cation, as well as its OH anion counterpart appear to remain within their hydration shells.[41] It is therefore these hydrated species that swell cellulose so extensively, that a real dissolution will result. The tight solvation shell of aqueous NaOH is believed to consist of around seven molecules of water

at room temperature, but at least two more molecules becomes inserted in this shell at 4 °C.[41] It is this solvated entity, together with probably less tightly bound water molecules, that are highly effective toward the swelling of cellulose. Indeed, it has been shown that it was at 0 °C and with an 8% NaOH solution that a maximum of water was adsorbed on cellulose.[2,46] For solubilizing cellulose, a dissolving agent must not only destroy the hydrogen-bonding network but also loosen the hydrophobic interactions that hold the cellulose sheets together within their crystalline environment. One can conceive that the low-temperature per-hydrated NaOH molecules can break the tight hydrogen bonding holding cellulose together, but it is not clear as how they will also pry open the cellulose sheets by loosening the hydrophobic interactions. The fact that there is no cellulose solubilization at high NaOH concentration, where the alkali hydration shell is reduced, would favor a dissolving system where it is the extensive swelling phenomenon that will be the driving force. How such a swelling will be sufficient to destructure the crystalline cellulose sheets remains to be demonstrated. It is our opinion that at present, a clear molecular mechanism remains to be deciphered to explain the dissolution of cellulose in the Q region.

The results presented in this study are essentially based on the interaction of microcrystalline cellulose from cotton with aqueous NaOH solutions. Under such conditions, these cellulose crystals are free to swell to yield the aforementioned Na−cellulose allomorphs when aqueous NaOH solutions of increasing concentrations penetrate the cellulose lattice. Other cellulose systems react somewhat differently from the present one, depending on their crystallinity, their ultrastructure, and the use or not of external constraints during NaOH impregnation. The variability of cellulose alkalization is illustrated in subjecting various cellulose samples to given NaOH solutions. For instance, samples of low crystallinity such as primary wall cellulose readily mercerize at only 9% NaOH,[47] whereas cotton requires 16%[2] and the highly crystalline *Valonia* cellulose cannot mercerize no matter what NaOH concentrations are applied.[48] Even with the same ramie cellulose sample, different Na−cellulose II allomorphs can be obtained, depending on the degree of sample constraints at equivalent NaOH concentrations.[9] The influence of constraint and its restriction on the swelling action is also reflected in the differences resulting from the slack versus tension mercerization of cotton.[2] The physical constraints created by the matrix of lignin is also responsible for the impossibility to fully mercerize lignified wood samples.[49] Given all this diversity, the phase diagram obtained with microcrystalline cellulose from cotton needs to be extrapolated with care to other native cellulose samples. In these, the intrinsic morphology or the inherent or applied constraints conditions may lead to different cellulose/NaOH/water equilibriums and therefore to different cellulose allomorphs. Here, this is well illustrated in comparing Figure 4, spectra 4A and 4A′, where two cellulose samples, differing not so much in crystallinity but rather in morphology, will yield NMR spectra that have substantial differences when subjected to identical NaOH treatment. It is thus clear that NMR studies such as the one presented here should be extended to a number of different cellulose samples if one wants to get the unified model of cellulose swelling and dissolution in aqueous NaOH.

Conclusions

The use of CP/MAS NMR experiments to analyze the polymorphism of Na−cellulose as functions of temperature and NaOH concentration leads to a reconsideration of the definition of the Na−cellulose complexes. It appears from these experiments that only two stable allomorphs can be distinguished within the whole phase diagram, namely, Na−cellulose I and Na−cellulose II. The possible assignment of a variety of other allomorphs is probably due to both the poor quality of their X-ray diffraction patterns and the coexistence of several phases, which may be more easily deconvoluted by NMR rather than by X-ray techniques.

The dissolution of microcrystalline cellulose in the so-called Q region pointed out by SP/MAS NMR has demonstrated the ability of NaOH to swell extensively the cellulose chain up to the complete dissolution under the Q conditions. In this region, however, the presence of topological constraints within samples of wood pulp apparently lead to a highly swollen state so-called Na−cellulose Q with a typical solid-state spectral signature.

In addition to the description of the phase diagram of the Na−cellulose complexes, this study illuminates the role of the Na^+ ions in the breakage of hydrogen bonds and the consequence of that breakage for the cellulose chain conformation. The NMR data nicely show the weakening of the hydrogen bonds with the increasing strength of the sodium ions and the transition between different cellulose chains configurations. In the Na−cellulose I complex, a first loosening of the hydrogen bond network leads to a relaxed backbone conformation and a *gt* position of the hydroxymethyl group similar to what is observed for disordered native cellulose. In a second step, the cellulose chain can relax even further to a conformation similar to what is observed in solution with a cellotriosyl repeat distance and a *gg* position of the hydroxymethyl group in the Na−cellulose II complex.

It is remarkable to note that these effects can be obtained by either increasing the soda concentration and/or decreasing the temperature, this latter effect being most probably related to the competition between the hydration of the Na^+ ion and its tendency to bind to the cellulose hydroxyls and, hence, to break the network of hydrogen bonds.

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