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# A Fourier transform infra-red spectroscopic analysis of the character of hydrogen bonds in amorphous cellulose

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Hydrogen-bonding formation in amorphous cellulose was characterized by the analysis of Fourier transform infra-red (*FT*i.r.) spectra. Films of regioselectively substituted methylcelluloses were used to model components of amorphous cellulose. An artificial infra-red (i.r.) spectrum for amorphous cellulose was quantitatively synthesized by a suitable mathematical combination of the i.r. spectra obtained for the methylcellulose model compounds. A comparison between the i.r. spectrum for an amorphous film blend composed of 2,3-di-*O*- and 6-*O*-methylcelluloses and the artificial spectrum showed an almost complete overlap in the OH frequency region, indicating that after mixing there is no interaction between the OH groups of each component in the film blend. In other words, the OH bands in the artificial spectrum were considered to be simply a sum of hydrogen-bond absorptions contributed by each individual spectrum. The artificial spectrum was then compared to an experimental spectrum for an amorphous cellulose sample. The difference between the two spectra (real–artificial) was then analysed and interpreted by using results from a previous i.r. study on hydrogen bonding in alcohols and our own assumptions about the probable hydrogen bonds formed in amorphous cellulose. These analyses revealed that while the hydroxyl groups at the C(2) and C(3) positions in a glucose repeating unit are isotropically involved in intermolecular hydrogen bonding in amorphous cellulose, the hydroxyl group at the C(6) position is favourably engaged in an interchain hydrogen bonding that results in the formation of a crystalline state. Thus we conclude that amorphous cellulose might be composed, at least to some extent, by randomly distributed domains formed by intermolecular hydrogen bonds.

**(Keywords: *FT*i.r. spectroscopy; amorphous cellulose; methylcelluloses)**

## INTRODUCTION

Kondo *et al.* have recently reported the synthesis of three regioselectively substituted methylcellulose compounds, namely 2,3-di-*O*-methylcellulose (23MC)[1], 6-*O*-methylcellulose (6MC)6[2] and tri-*O*-methylcellulose (236MC)[3] (*Figures 1b*, *c* and *d*, respectively). Since the methylcelluloses prepared had a controlled distribution of substituents, and thus hydrogen bonds, they were considered to be model compounds for amorphous cellulose and hence ideal for examining the relationship between the polymer structure and physical properties of cellulose and its derivatives in terms of hydrogen-bond formation.

In our previous studies in this series, *FT*i.r. (Fourier transform infra-red) spectroscopy was used to identify[4] intra- and intermolecular hydrogen bonds in the regioselectively synthesized 23MC and 6MC, as well as to investigate the nature of hydrogen-bond interactions in cellulose–synthetic polymer blends[5]. These studies indicated that films of 23MC and 6MC exhibited narrow OH stretching bands in their i.r. spectra because of controlled hydrogen bonding, thus OH band shifts due to different hydrogen-bond interaction in the blends are distinguishable. Morphologically, films cast from these methylcellulose derivatives were also found to be predominantly amorphous rather than crystalline. Therefore, the narrow OH absorbance bands and the amorphous homogeneity of the sample microstructure enabled us to clarify and classify the interchain hydrogen-bond interactions found in our samples. In this present paper, we believe that a characterization of the hydrogen bonds found in amorphous cellulose would be of fundamental value. Furthermore, we propose that a structural study of amorphous cellulose in the light of hydrogen bonding might be a first step towards uncovering details of how molecules rearrange in going from the liquid to the crystalline state.

Amorphous cellulose samples are usually prepared by ball milling of cellulose[6,7], by deacetylation of cellulose acetate with sodium methoxide in anhydrous methanol[8], or by precipitation from non-aqueous solvent systems into non-aqueous regeneration media with the avoidance

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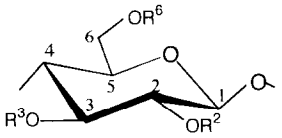



| | $R^2$ | $R^3$ | $R^6$ |
|---|---|---|---|
| (a) | H | H | H |
| (b) | $CH_3$ | $CH_3$ | H |
| (c) | H | H | $CH_3$ |
| (d) | $CH_3$ | $CH_3$ | $CH_3$ |

**Figure 1** Cellulose film sample structures: (a) cellulose; (b) 2,3-di-*O*-methylcellulose (23MC); (c) 6-*O*-methylcellulose (6MC); (d) tri-*O*-methylcellulose (236MC)

of stress[9–13]. To date, most of these samples have been studied by wide-angle X-ray diffraction (WAXD)[6–14], *FT*i.r. spectroscopy[14], and solid-state nuclear magnetic resonance (n.m.r.) spectroscopy[13]. However, none of these studies have looked at amorphous cellulose in terms of the hydrogen bonds that are formed. Only Hatakeyama *et al.*[15] have previously reported on the formation of interchain hydrogen bonds with increasing temperature for amorphous regions in cellulose fibres.

In this present report, we have tried to analyse and comment on the types of hydrogen bonds formed in amorphous cellulose. Our methodology here has been threefold: (1) to quantitatively produce an artificial i.r. spectrum for amorphous cellulose by using a combination of the spectra of amorphous methylcellulose model compounds, (2) to characterize the difference between the real and the artificial spectra in terms of the formation of hydrogen bonds and, finally, (3) to compare the results of (2) with i.r. spectra of propyl alcohol situations, which can serve as model systems for intermolecular hydrogen bonding. This approach allowed us to draw a number of conclusions about the hydrogen bonds formed at the C(2) and C(3) positions in the anhydroglucose repeating units of amorphous cellulose.

## EXPERIMENTAL

### *Materials*

The polymer materials 23MC (*Figure 1b*), 6MC (*Figure 1c*) and 236MC (*Figure 1d*) were prepared by using the methods outlined in our previous papers[1–3,5]. Each polymer was found to have a uniform structure. G.p.c. (gel permeation chromatography) elution curves, which were calibrated with polystyrene standards (*Table 1*), were used to calculate the weight-average molar mass for each sample. A bleached sulfite pulp with a degree of polymerization of 935 was used as the pure cellulose sample. HPLC-grade *N*,*N*-dimethylacetamide (DMAc), methanol and chloroform (Aldrich Chemical Co.) were used as solvents without further purification.

**Table 1** Characterization data for the four cellulosic homopolymer samples[a]

| Sample | $M_w$ | Density ($g\,cm^{-3}$) |
|---|---|---|
| Cellulose | $1.2 \times 10^5$ | 1.50 |
| 23MC | $4.0 \times 10^4$ | 1.30 |
| 6MC | $3.5 \times 10^4$ | 1.30 |
| 236MC | $4.6 \times 10^4$ | 1.27 |

[a] All samples in the form of amorphous films

### *Sample preparation*

The methylcellulose homopolymers of 23MC, 6MC and 236MC were dissolved separately in methanol/chloroform (1/4 vol/vol), DMAc, and chloroform, respectively; the concentration was 0.8 wt% in each case. All solutions were filtered and then stored in closed containers.

Each solution was stirred for more than 3 days and films were then cast from the solutions as follows: 1 g of each solution was poured into a flat-bottomed tray and heated to 50°C under reduced pressure for 3 days. The solvent was then evaporated to produce an as-cast film. The resulting film was dried for 2 more days under high vacuum at 50°C in order to completely remove any residual solvent, and was then stored in a desiccator. Pure cellulose film was cast from LiCl DMAc solution[16] including about 1.0% cellulose. The films were subsequently washed with ethanol (dried over molecular sieves) and then allowed to dry. A blend film of 23MC and 6MC (1.08/1 wt/wt) was also prepared in the same manner. All the films prepared in this study were sufficiently thin (5 $\mu$m) to obey the Beer–Lambert law[17]. Moreover, from WAXD measurements the films were found to be predominantly amorphous in character (described in the following section).

The density of the four cellulosic homopolymer films was measured by using pycnometry; a mixed medium of *p*-xylene/carbon tetrachloride was used for pure cellulose, 23MC and 6MC, while methyl ethyl ketone/iodoethane was used for 236MC. Characterization data for the prepared cellulosic films are listed in *Table 1*.

### *Measurements*

Wide-angle X-ray diffraction patterns were recorded by computer using nickel-filtered CuK$\alpha$ radiation (50 kV and 120 mA) produced by a JEOL JDX-8200 X-ray generator. The small-angle X-ray scattering (SAXS) intensity distribution was recorded with a Rigaku RU-300 X-ray generator equipped with a position-sensitive proportional counter (PSPC). *FT*i.r. spectra were recorded using a Perkin-Elmer 1720X FTIR spectrometer. A total of 64 scans with a 2 $cm^{-1}$ resolution were signal-averaged and stored; the wavenumber region investigated ranged from 4000 to 400 $cm^{-1}$. A KBr solution cell (New Jersey Crystal Co.) with a 0.5250 mm pathlength was used for liquid samples; the concentration of the latter was 4 wt% in carbon tetrachloride.

The synthesized i.r. spectrum (henceforth referred to as the artificial spectrum) for amorphous cellulose was quantitatively constructed by the adding or subtracting of a suitably multiplied* spectrum of each homopolymer sample film having the same thickness.

## RESULTS AND DISCUSSION

### *WAXD characterization*

Wide-angle X-ray diffraction (WAXD) patterns for cellulose (A), 23MC (B), 6MC (C) and the blend of 23MC and 6MC (D) films are shown in *Figure 2*. The pure cellulose WAXD pattern (A) exhibited a diffused scattering, indicating an amorphous microstructure. The

* Value explained in the Appendix

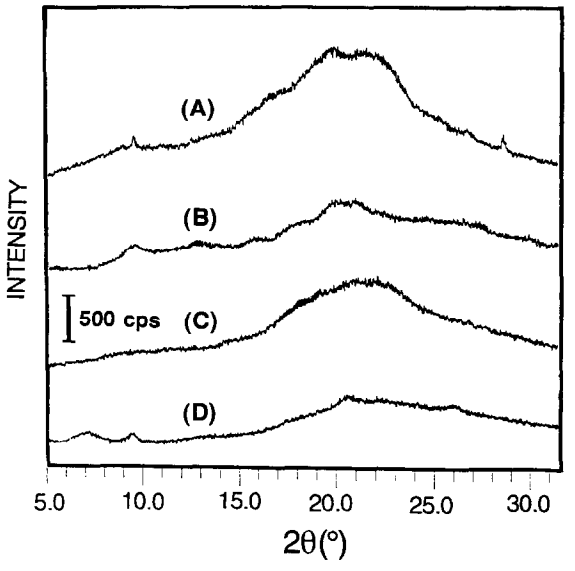



**Figure 2** Wide-angle X-ray diffraction patterns for cast films: (A) cellulose; (B) 23MC; (C) 6MC; (D) blend of 23MC and 6MC (1.08/1 wt/wt)

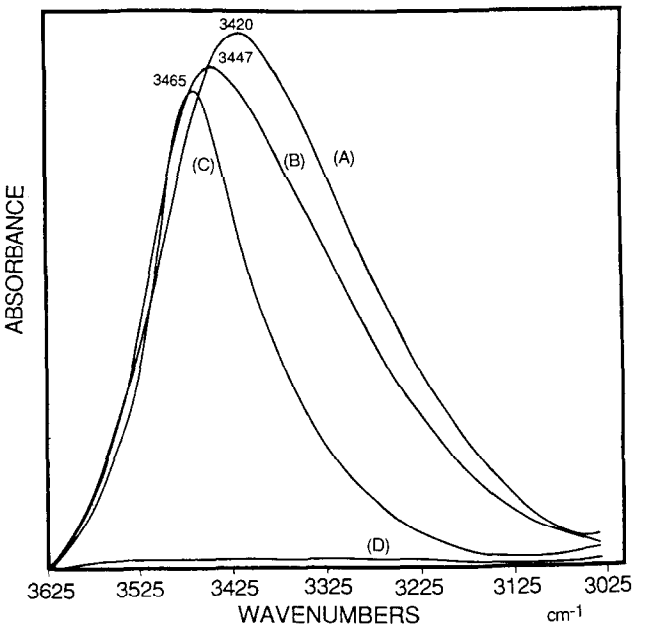



**Figure 3** I.r. spectra obtained for amorphous film samples in the OH frequency region: (A) cellulose; (B) 23MC; (C) 6MC; (D) 236MC

methylcellulose cast films also showed these diffuse diffraction patterns, indicating that they too had a predominantly amorphous structure.

*Synthesis of the artificial i.r. spectrum for amorphous cellulose*

Currently there is a shortage of structural information about amorphous cellulose because methods for this characterization have been limited to WAXD and cross-polarization/magic angle spinning (CP/MAS) $^{13}C$ nuclear magnetic resonance (n.m.r.) spectroscopy. We considered it vital to identify the types of hydrogen bonds present in amorphous cellulose in order to completely characterize it structurally. At present *FT*i.r. spectroscopy is one of the best techniques available for deriving structural information about hydrogen bonding. Consequently, i.r. spectra were recorded for all of the prepared films which proved to be highly amorphous by WAXD measurements. These four i.r. spectra were combined mathematically in the correct proportions to produce an artificial i.r. spectrum which could then be compared to a real spectrum for amorphous cellulose. Our proposal here, for the artificial spectrum, is that the OH band is simply a linear combination of its component contributions, including hydrogen-bond interactions, and that subtraction of the artificial spectrum from the real spectrum can provided some information about the type of hydrogen-bond interactions in the real cellulose spectrum. For a comparison of this sort to be successful the path length of the cell must be altered to compensate for changing concentrations, because the same number of absorbing molecules should be present in the infra-red beam at each concentration[18]. Therefore, we have made the following assumptions for the artificial spectrum: (1) it is only applicable for the amorphous state of the sample and (2) the irradiated volume in the light path is identical for all of the samples because all four films are of a uniform thickness (5 $\mu$m). Each spectrum was manipulated by applying the above assumptions: namely, a mole value of each of the three hydroxyl groups at the C(2), C(3) and C(6) positions should be adjusted to give equally one per glucose unit in the light path and the density of glucose units in the recorded spectrum should be adjusted to that of the amorphous cellulose prepared from the LiCl–DMAc solution. In the light of the above assumptions, the following equation was derived:

$$\text{Artificial Spec(Amocell)} = \alpha(\text{Spec(6MC)} + \beta\text{Spec(23MC)} - \gamma\text{Spec(236MC)}) \quad (1)$$

where $\alpha = 1.25$, $\beta = 1.08$ and $\gamma = 1.19$; Spec and Amocell refer to the spectrum and amorphous cellulose, respectively. The calculation used to determine the values $\alpha$, $\beta$, and $\gamma$ is described in the Appendix.

*Figure 3* shows the OH frequency region of the i.r. spectra for each amorphous homopolymer film sample investigated. By using these four spectra and by quantitatively applying equation (1), we were able to construct the artificial spectrum illustrated in *Figures 4b* and

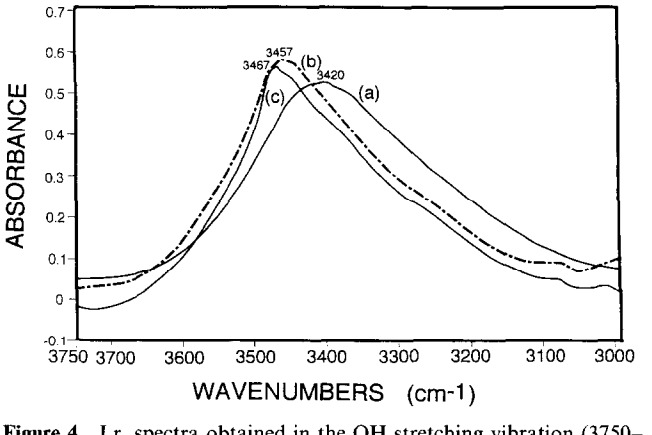



**Figure 4** I.r. spectra obtained in the OH stretching vibration (3750–3000 $cm^{-1}$) region: (a) real spectrum of amorphous cellulose film; (b) artificial spectrum; (c) spectrum for the blend sample (23MC/6MC = 1.08/1 wt/wt)

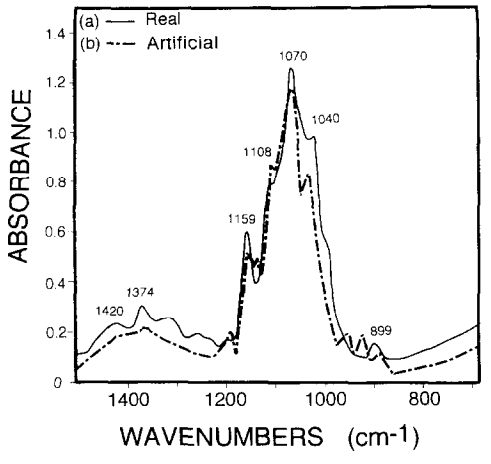



**Figure 5** I.r. spectra in the C–O stretching vibration (1500–700 $cm^{-1}$) region: (a) real cellulose spectrum; (b) artificial cellulose spectrum

**Table 2** Comparison of typical absorption band frequencies for the real and the artificial i.r. spectra of amorphous cellulose

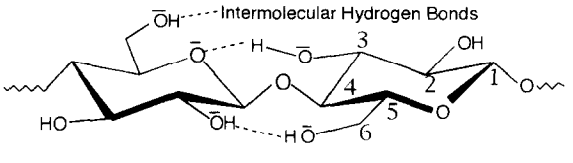
| Frequency ($cm^{-1}$) | | | |
|---|---|---|---|
| Real[a] | Artificial[b] | Relative intensity[c] | Interpretation[18] |
| 669 | 671 | W | OH out-of-plane bending |
| 899 | 892 | M | Antisymmetric out-of-phase ring stretching |
| 1070 | 1075 | S | Skeletal vibrations involving C–O stretching |
| 1159 | 1154 | S | Antisymmetric bridge C–O–C stretching |
| 1374 | 1375 | M | CH bending |
| 1420 | 1425 | W | $CH_2$ symmetric bending |
| 2892 | 2903 | M | CH stretching |
| 3420 | 3457 | S | OH stretching |

[a] Real spectrum for an amorphous cellulose cast film
[b] Artificial spectrum for amorphous cellulose
[c] S, strong; M, medium; W, weak

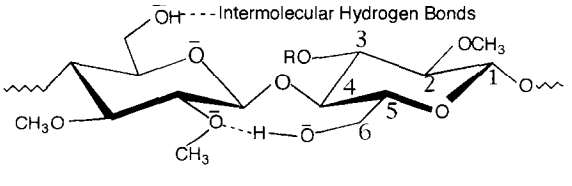
*5b*. The i.r. spectrometer software produced a list of the most prominent bands in this artificial i.r. spectrum in the region being studied, with *Table 2* showing the most probable assignment for these bands, as well as those found in a real amorphous cellulose sample. *Figures 4* and *5*, respectively, show the OH and C–O stretching vibration regions resulting from the glucose ring skeletal vibration. In comparing the real and the artificial spectra for the amorphous cellulose, there is no significant difference in the ring stretching vibration region, as clearly illustrated in *Figure 5*. This would seem to suggest that subtraction of the $\gamma$Spec(236MC) term in equation (1) may preclude any absorption contributions by methyl groups in the methylated samples to the ring stretching vibrations. Thus, the artificial spectrum mirrors the glucose ring structure found in real amorphous cellulose. The data contained in *Table 2*, which lists typical absorption frequencies for the two spectra, also seem to support this hypothesis. This *FT*i.r. result shows that the OH groups in the anhydroglucose units, despite being blocked by methyl groups, do not affect the structure of the glucose ring. In other words, methyl blocking by the hydroxyl groups in cellulose can be useful in controlling the formation of hydrogen bonds without causing a resultant change in the glucose ring conformation. Thus this study has been proven to give a satisfactory model compound for cellulose. With regard to the stretching and bending vibrations for the methane and methylene groups in cellulose, our quantitative mathematical model could not completely remove the contribution by the methyl groups in our methylated samples so as to totally match the artificial spectrum of amorphous cellulose.

The marked differences in the OH stretching vibration region of the i.r. spectra result from a variety of hydrogen bonds (*Figure 4*) and these differences were also slightly observed in the CH stretching and CH bending regions because of the methyl contributions. In this paper we will limit our discussion to interpreting the OH absorption bands in terms of hydrogen-bond formation. In our previous report[4], 6MC showed a very narrow and symmetric OH absorption band which was attributed to two intramolecular hydrogen bonds (*Figure 6c*): one between the OH at the C(3) position and its neighbouring ring oxygen (O(5)) and the second between the OH at the C(2) position and the ether oxygen of $OCH_3$ at the C(6) position. Alternatively, the OH groups at the C(6) position in 23MC could be involved in either intra- or intermolecular hydrogen bonding with the $OCH_3$ at the C(2) position, as illustrated in *Figure 6b*. There are also very few 'free' OH groups in both 23MC and 6MC, suggesting that almost all of the OH groups are engaged in some type of hydrogen bonding. Possible hydrogen bonds formed at the individual positions of the glucose ring (C(2), C(3) and C(6)), including those described

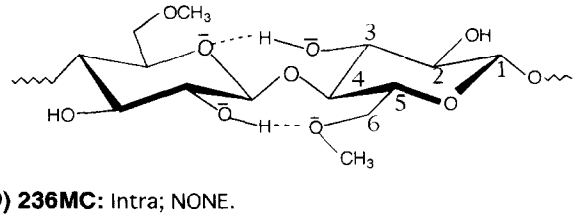
**(A) Cellulose:** Intra; OH at C-2 and OH at C-6, OH at C-3 and O in the neighboring ring.
Inter; OH at C-2, C-3 and C-6.




**(B) 23MC:** Intra; OH at C-6 and OCH3 at C-2.
Inter; OH at C-6.




**(C) 6MC:** Intra; OH at C-3 and O in the neighboring ring, OH at C-2 and OCH3 at C-6.
Inter; NONE.




**(D) 236MC:** Intra; NONE.
Inter; NONE.

**Figure 6** Possible hydrogen bonds, formed at the individual C(2), C(3), and C(6) positions, of a glucose ring in amorphous cellulose

above, are illustrated in *Figure 6* for cellulose, 23MC, 6MC and 236MC. When the artificial spectrum (trace (b) in *Figures 4* and *5*) was constructed by adding the two spectra, B and C in *Figure 3*, and subtracting spectrum D according to equation (1), it was assumed to include the simple sum contributions from the absorption bands due to hydrogen bonding in 23MC and 6MC, namely three OH bands due to intramolecular hydrogen bonding at each of the C(2), C(3), and C(6) positions, as well as any intermolecular hydrogen bonding at the C(6) position.

Trace c in *Figure 4* shows the OH stretching vibration for the film blend of 23MC and 6MC. This film proved to be highly amorphous, as shown in *Figure 2D*. Interestingly, trace c also showed almost a complete overlap with the artificial spectrum (trace b), in both peak shape and absorbance (*Figure 4*). Since the spectrum in trace b was synthesized by simply adding both the 23MC and the 6MC spectra, it should not therefore, contain any signals due to hydrogen-bond interactions between the 23MC and 6MC. We thus concluded that the spectrum of the film blend showed no component OH group interactions after mixing. This good agreement between the two spectra also proves that our mathematical method (equation (1)) used in constructing the artificial spectrum for amorphous cellulose is valid.

*Difference between the real and the artificial spectra*

In the real spectrum of amorphous cellulose, both intra- and intermolecular hydrogen bonds (*Figure 6a*) may be possible if we take into account contributions from the crystalline portions of the cellulose[14,19,20]. As described previously, there is a marked difference in the OH stretching region of the real and the artificial i.r. spectra. The difference spectrum (real–artificial; *Figure 4a–Figure 4b*) is shown in *Figure 7* with the region between 3750 and 3000 $cm^{-1}$ expanded to clearly show this marked difference. Considering that the artificial spectrum was constructed by assuming a linear contribution by the intra- and intermolecular hydrogen bonds at the C(6) position, as already explained, the difference spectrum should thus contain peaks arising from intermolecular hydrogen bonds at the C(2) and C(3) positions and any 'free' hydroxyl groups. Of course, the bands resulting from common hydrogen bonds in both the real and the artificial spectra are not completely cancelled out by subtraction because in the two spectra the magnitude of each OH absorbance band is not necessarily of equal value. The difference spectrum can thus include, to a greater or lesser extent, all of the hydrogen bonds present in pure amorphous cellulose. However, the marked differences in the two spectra cannot adequately be explained simply in terms of unequal contributions from common hydrogen bonds: the two positive peaks and the negative valley in the difference spectrum are attributed to intermolecular hydrogen bonds at the C(2) and C(3) positions, as well as 'free' OH groups.

The main peaks in *Figure 7* appeared at two specific wavenumbers, namely 3472 and 3352 $cm^{-1}$. Usually unbonded or 'free' OH groups absorb infra-red light at 3584 to 3650 $cm^{-1}$, which is at a higher wavenumber than observed for our two peaks[4,18]. A shoulder around 3580 $cm^{-1}$ with an absorption of −0.06 may be due to the 'free OH' groups. As mentioned earlier, since all of the OH groups in 23MC and 6MC are engaged in some form of hydrogen bonding[4], the artificial spectrum formed by combining the two contributing spectra is thought to have few 'free' OH groups. Therefore, the almost negligible signal at 3580 $cm^{-1}$ in the difference spectrum indicates that there are very few 'free' OH groups in the amorphous cellulose itself. A negative absorbance value at 3472 $cm^{-1}$ indicates that the signal was 'over-cancelled' in the artificial spectrum, while the positive band at around 3352 $cm^{-1}$ was attributed to the intermolecular hydrogen bonding at the C(2) and C(3) positions.

In order to clarify the hydrogen-bond formation and band assignment at 3352 and 3472 $cm^{-1}$, n-propyl (containing a primary OH) and isopropyl (containing a secondary OH) alcohols were chosen as models for the OH groups. As noted in our earlier papers[4,5], hydrogen bonding between the ether oxygens (electron donors) and OH groups (electron acceptors) is thought to be quite

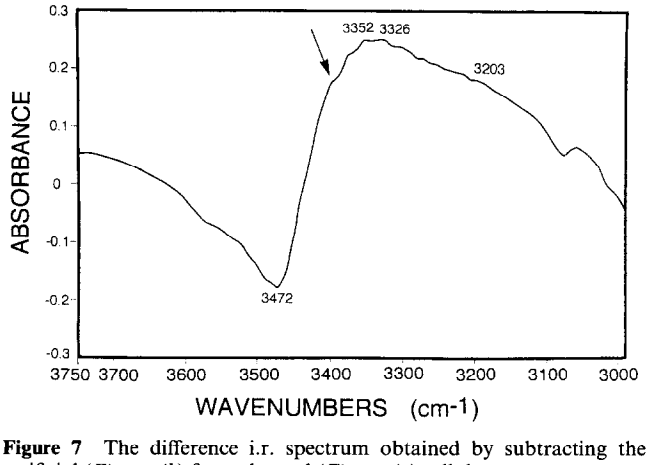



**Figure 7** The difference i.r. spectrum obtained by subtracting the artificial (*Figure 4b*) from the real (*Figure 4a*) cellulose spectra

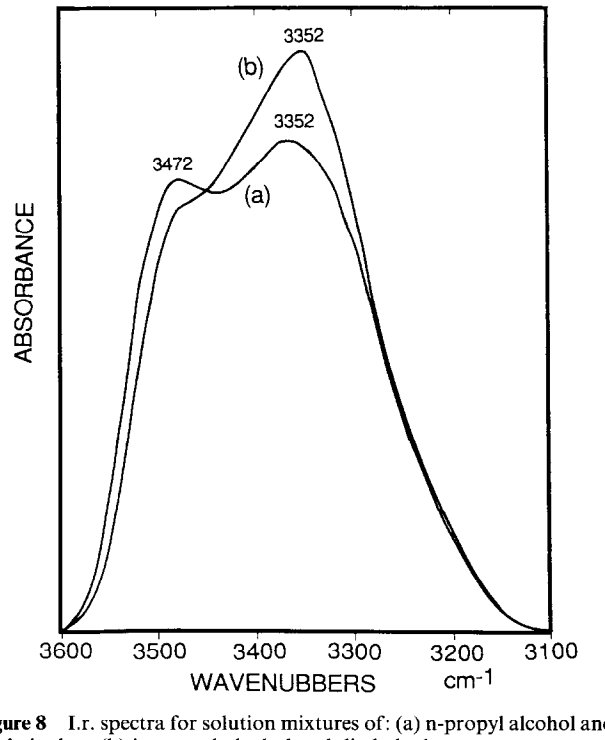



**Figure 8** I.r. spectra for solution mixtures of: (a) n-propyl alcohol and diethyl ether; (b) isopropyl alcohol and diethyl ether

favourable. This phenomenon was also observed in a mixture of the alcohols with diethyl ether. *Figure 8* shows the OH frequency regions of the i.r. spectra of just two such mixtures. Pure n-propyl alcohol and isopropyl alcohol gave the same OH absorption peaks at around 3352 $cm^{-1}$. This absorption band is attributed to intermolecular hydrogen-bond formation between the alcohol molecules. After mixing each alcohol with an ether, a new band (at 3472 $cm^{-1}$) appeared in both spectra, as shown clearly in *Figure 8*, indicating that both primary and secondary OH groups can engage in hydrogen bonding with the ether oxygen in diethyl ether. Moreover, the wavenumbers for the two bands in the mixtures coincided with the two bands found in the difference spectrum (*Figure 7*). The positive absorption band at 3352 $cm^{-1}$ in the difference spectrum was located in exactly the same position as the OH bands for the two alcohols shown in *Figure 8*. The negative absorption valley at 3472 $cm^{-1}$ was at the same wavenumber as the shifted band attributed to hydrogen bonding between the ether oxygen and the alcohol OH group in the mixture. Thus the OH groups involved in hydrogen bonding with the oxygens showed a shift to a higher wavenumber and were found to be in a similar position to the OH groups forming intramolecular hydrogen bonds in 6-*O*-methylcellulose[4].

The good agreement between the band positions in the pure alcohols and mixtures of the alcohols with ethers and the positive band at 3352 $cm^{-1}$ in the difference spectrum (*Figure 7*) clearly indicated that this must be due to intermolecular hydrogen bonding at the C(2) and C(3) positions. The negative valley (3472 $cm^{-1}$) in the difference spectrum appeared to reflect an excess of hydrogen bonds, either at the C(2) position and the $OCH_3$ at the C(6) position, or at the C(6) position and the $OCH_3$ at the C(2) position in the artificial spectrum. This indicates that the intermolecular hydrogen bonds at the C(2) and C(3) positions in amorphous cellulose probably exhibit a similar isotropic behaviour to that of the intermolecular hydrogen bonds in the alcohols.

*State of amorphous cellulose*

In the previous section we have characterized the OH groups at the C(2) and C(3) positions in amorphous cellulose. The role of the other primary OH group located at the C(6) position in forming amorphous cellulose was also investigated. *Figure 9* shows the WAXD patterns, (a) and (b), for 23MC films cast from two different solutions, namely methanol/chloroform (1/4 vol/vol) and DMAC, respectively. It is clearly evident that film (a) was predominantly amorphous in character while film (b) was mostly crystalline. This shows that as the solvent is changed for the same 23MC sample, the crystallinity of the film varies from solvent to solvent and the OH groups at the C(6) position may be favourably involved in intermolecular hydrogen bonding. The extent of crystallization may be dependent upon the behaviour of the primary OH group located at the C(6) position. Stated differently, the OH group at the C(6) position may be significant in determining the final morphological make-up of cellulose. We propose that when the C(6) hydroxyl groups in cellulose are, to a great extent, engaged in the intermolecular hydrogen bonding the resulting cellulose should exhibit higher crystallinity. Invoking this hypothesis, and the results obtained about the C(2) and C(3) hydroxyl groups for amorphous cellulose in the previous section, either a random distribution of microcrystallites or a series of domains arising from intermolecular hydrogen bonds will result in a highly amorphous state for cellulose. To confirm the existence of these postulated microcrystallites, SAXS intensity distributions were measured using the PSPC system. The SAXS pattern for amorphous cellulose showed no significant scattering maxima, indicating that there was no lamella structure present in the cellulose. Thus the SAXS and WAXD patterns for amorphous cellulose gave no support to the idea that microcrystallites were present. We therefore concluded that amorphous cellulose must include, to some degree, domains formed by the intermolecular hydrogen bonds at the C(2), C(3) and C(6) positions. In addition, when the amorphous wet gel-like swollen film was cast from a LiCl–DMAC cellulose solution and was then subjected to tensile drawing operations, the draw ratio that was reached was at most ca. 2.0 and, instead of showing a high degree of orientation (which is characteristic of crystalline domains), the density of the film did not change[21]. This behaviour was attributed to the formation of intermolecular hydrogen bonds[22], and gave us further support for our proposed hypothesis.

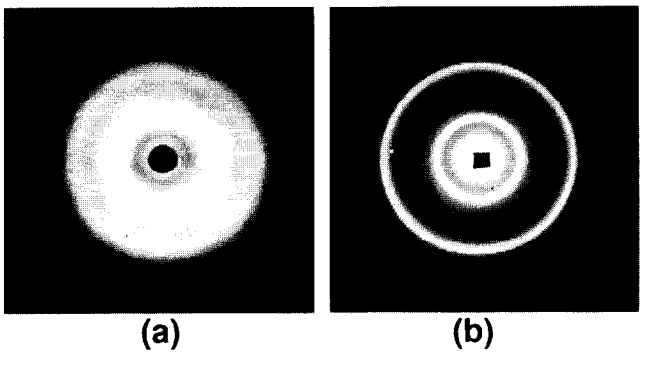



**Figure 9** WAXD patterns obtained for the same 23MC films cast from different solutions: (a) methanol/chloroform (1/4 vol/vol); (b) DMAc

Thus far we have tried to explain the i.r. spectra of cellulose in terms of the behaviour of the C(2) and C(3) position hydroxyl groups, but have omitted any speculation about the intermolecular hydrogen bonds at the C(6) position. If the C(6) hydroxyl groups are involved in intermolecular hydrogen bonding, then an absorption band reflecting this should appear in the i.r. spectrum. However, the i.r. band representing intermolecular hydrogen bonds at the C(6) position should appear at almost the same position as the OH band found in 23MC (3447 $cm^{-1}$; trace B in *Figure 3*). Indeed, by re-examining the difference spectrum shown in *Figure 7*, we can see a very small shoulder at approximately 3447 cm (indicated by an arrow in this figure).

## CONCLUSIONS

It is important to characterize the type of hydrogen bonds formed in cellulosic molecules in order to clarify the correlation between structure and physical properties. In this paper, we particularly wanted to examine in detail the formation of hydrogen bonds in amorphous cellulose because this has not previously been carried out. The regioselectively substituted amorphous cellulose derivatives, 6-*O*-, 2,3-di-*O*-, and tri-*O*-substituted methylcellulose, were used to model the components of

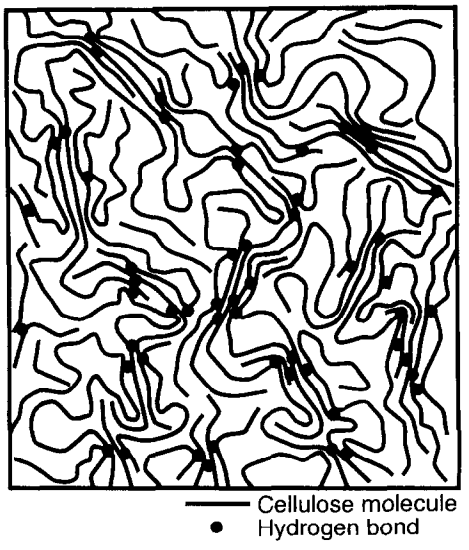



**Figure 10** Schematic model proposed for amorphous cellulose

amorphous cellulose. An artificial spectrum for amorphous cellulose was then quantitatively constructed mathematically by using the model compound i.r. spectra to investigate hydrogen-bond formation in cellulose. First, it was shown that the intermolecular hydrogen bonds at the C(2) and C(3) positions exhibit a behaviour which was very similar to that found in model alcohol compounds. This suggested that the intermolecular hydrogen bonds may be distributed isotropically. Secondly, the primary OH group at the C(6) position appeared to play a crucial role in determining the crystallization state for cellulose.

These two observations led us to the following conclusion. The type of intermolecular hydrogen bonds found at the C(2), C(3) and C(6) hydroxyl group positions is participating, to some extent, in determining the structure of amorphous cellulose. In the light of the above observations and the results from SAXS, amorphous cellulose is believed to be composed of randomly distributed domains involving intermolecular hydrogen bonds. We therefore propose a model for amorphous cellulose in which some amorphous domains are partly interacted by intermolecular hydrogen bonds, as illustrated in *Figure 10*.

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## APPENDIX

Equation (1) was derived in the following manner, based on the two assumptions outlined in the main text.

The molar numbers of glucose units in the i.r.-irradiated volume, $v$, was $(1.50v/162)$, $(1.30v/190)$, $(1.30v/176)$, and $(1.27v/204)$ for cellulose, 23MC, 6MC, and 236MC, respectively. The denominator is the molar mass for a glucose unit in each of the four compounds while the density value, $\rho$, for each film sample appears in the numerator. The bracketed term on the right-hand side of equation (1) represents the absorbance value for a spectrum of amorphous cellulose containing $(1.30v/176)$ moles of glucose units of 6MC in an irradiated volume $v$. Thus, a spectrum of amorphous cellulose requiring $(1.50v/162)$ moles of glucose units should be made with $\alpha = (1.50v/152)/(1.30v/176) = 1.25$. Here, we focus on the amount of OH groups as defined in the bracketed term. As both 23MC and 6MC have one hydroxyl group at the C(6) position and two hydroxyl groups at the C(2) and C(3) positions per glucose unit, respectively, amorphous cellulose having $(1.30v/176)$ moles of glucose units in a volume $v$ contains one equivalent of OH groups in 6MC and $\beta$ equivalent in 23MC; $\beta = (1.30v/176)/(1.30v/190) = 1.08$. After this calculation has been carried out, an excess of $(1.30v/176)$ moles of glucose rings in 6MC are present. To balance this excess addition of rings, a corresponding $\gamma$ amount of 236MC was subtracted. Therefore, $\gamma$ is $(1.30v/176)/(1.27v/204)$, or 1.19.