

# Characterization of Ethylcellulose with Different Degrees of Substitution (DS): A Diffuse-Reflectance Infrared Study

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## Résumé

Nous avons étudié les particularités structurales des polymères de l'éthylcellulose par spectroscopie FTIR en mode de réflectance diffuse. Nous avons tenté de développer une corrélation entre les paramètres structurels, tel que le degré de substitution (DS soit le nombre moyen de groupements hydroxyles substitués par l'agent étherifiant) et le profil de la bande d'étirement OH. La spectroscopie infrarouge des polymères de l'éthylcellulose a montré une bande étroite à  $2900\text{ cm}^{-1}$ , associée avec une vibration d'étirement CH, et une bande plus large à une longueur d'onde plus grande qui correspond aux modes d'étirement de OH. La bande OH est elle-même constituée de deux composantes centrées à  $3500\text{ cm}^{-1}$  (bande I) et  $3300\text{ cm}^{-1}$  (bande II). L'intensité de la bande I était indépendante du DS et a été attribuée à une vibration d'étirement des groupements hydroxyles liés aux positions C1 et C4 des cycles anhydroglucose terminaux. L'intensité de la bande II augmente largement avec une diminution du DS et correspond à la vibration des groupements OH non substitués aux positions C2, C3 et C6 du cycle. L'effet du DP sur la bande d'étirement OH est négligeable, DP représentant le nombre d'unités d'anhydroglucose dans la chaîne, au moins dans la gamme de valeurs de DP étudiée dans ce travail.

## Abstract

*The structural features of ethylcellulose polymers*

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were studied by FTIR spectroscopy in the diffuse reflectance mode. Attempts to develop a correlation between structural parameters, such as the degree of substitution (DS, the average number of hydroxyls substituted by the etherifying agent) and the OH stretching band profile, were made. Infrared spectroscopy of ethylcellulose polymers showed a sharp band at  $2900\text{ cm}^{-1}$ , associated with a CH stretching vibration, and a broader band at higher wavenumber, which corresponds to OH stretching modes. The OH band is in turn comprised of two components centred at  $3500\text{ cm}^{-1}$  (band I) and  $3300\text{ cm}^{-1}$  (band II). The intensity of band I was insensitive to the DS and was attributed to the stretching vibration of hydroxyl groups bonded to C1 and C4 positions of terminal anhydroglucose rings. The intensity of band II increases greatly with decreasing DS and corresponds to the vibration of non-substituted OH groups at C2, C3 and C6 ring positions. The effect of DP on the OH stretching band is negligible, where DP equals the number of anhydroglucose units in the chain, at least in the range of DP values studied in this work.

**Keywords:** Cellulose ether, degree of substitution, infrared spectroscopy, deconvolution, OH and CH stretching vibration

## Introduction

Cellulose is the most abundant and widely used organic material in the world, with a worldwide consumption that is higher than steel, coal, cereals or sugar (1). Cellulose can be converted to useful derivatives by etherification of the various ring hydroxyl groups. A variety of cellulose

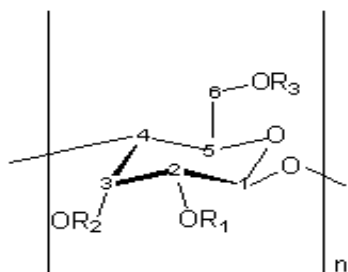


Figure 1. Cellulose structure.

Table 1. Different possibilities of substitution of cellulose to obtain ethylcellulose

	DS	R1	R2	R3
	0	H	H	H
ETHYLCELLULOSE	1	H	H	CH <sub>2</sub> -CH <sub>3</sub>
	2	H	CH <sub>2</sub> -CH <sub>3</sub>	CH <sub>2</sub> -CH <sub>3</sub>
	3	CH <sub>2</sub> -CH <sub>3</sub>	CH <sub>2</sub> -CH <sub>3</sub>	CH <sub>2</sub> -CH <sub>3</sub>

ether derivatives are manufactured annually at an industrial scale. These chemicals include carboxymethylcellulose (CMC), cyanoethylcellulose (CEC), ethylcellulose (EC), methylcellulose (MC), hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), and mixed ethers such as hydroxypropylmethylcellulose (HPMC), carboxymethylhydroxyethylcellulose (CMHEC), and hydroxymethylcellulose (HEMC) (2). Cellulose ethers are routinely used in very different fields, such as food and drugs manufacturing, oil-well drilling (2) or artwork conservation (3).

A variety of experimental techniques have been widely applied to characterise cellulose and its derivatives. They include FTIR and UV-vis spectroscopies, solid-state <sup>13</sup>C NMR, X-ray diffraction, thermal analysis and viscosity measurements. These techniques were employed to investigate the characteristics of native and purified cellulose (4,5) and the rheological properties of aqueous cellulose suspensions (6), as well as the structure and properties of cellulose ethers (mainly methylcellulose) (7-13). Kondo *et al.* (7-12) derived valuable structural information on cellulose polymers when studying the influence of alkyl and allyl substituents at C2, C3 and C6 positions (see figure 1 and table 1) on specific inter- and intramolecular hydrogen bonding. They used FTIR spectroscopy to distinguish between both types of

Table 2. DS values of the products used in the study

ABBREVIATION	DS
EC1	2.7
EC2	2.9
EC3	2.9
EC4	2.9
EC5	2.9
EC6	3.0
EC7	3.0
EC8	3.0

hydrogen bonds in alkylcelluloses, particularly regioselectively synthesized 2,3-methylcellulose and 6-methylcellulose (7,10,11). Moreover, FTIR spectroscopy, together with solid-state <sup>13</sup>C NMR and gas-liquid chromatography, was successfully applied to monitor the substituents distribution in cellulose chains, allowing a method for the regioselective synthesis of the alkyl celluloses to be developed (9).

Given the importance of the degree of substitution (DS) as a characteristic factor of a polymer, and due to the fact that this is not usually specified by suppliers of commercial ethylcellulose specifications, the use of fast and reliable instrumental techniques and methods to measure this parameter and to correlate it to the chemical and molecular structure of the chains would be extremely helpful at both fundamental and applied levels.

In this work, our interest is focused on the use of IR spectroscopy in the characterization of ethylcellulose samples and on checking the sensitivity of the IR spectral response against the degree of substitution (DS) and the degree of polymerization (DP) variations.

## Experimental

### Materials

Ethylcellulose was supplied by Dow Chemical Company. Table 2 shows the DS of the different commercial products used (14). It should be stressed here that ethylcellulose with a DS value lower than 2.7 is not commercially available, as has been pointed out by others (2,15). Cellulose was supplied by Fluka. KBr (IR grade) was supplied by Aldrich.

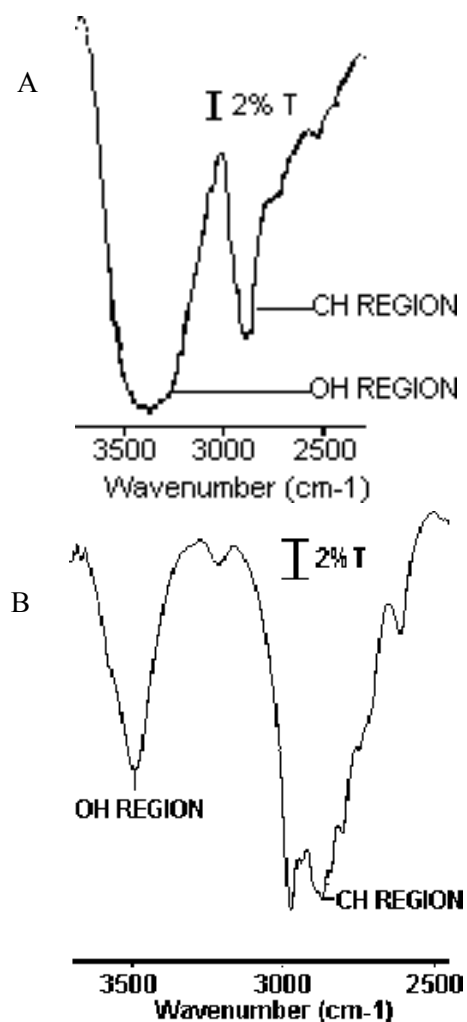


Figure 2. A) Cellulose IR spectrum in the 3700 – 2500  $\text{cm}^{-1}$  range; B) EC7 IR spectrum in the 3700 – 2500  $\text{cm}^{-1}$  range

#### Infrared spectra measurements

The infrared experiments were performed using a Nicolet Magna 550 spectrometer equipped with a DTGS detector and a Spectra Tech diffuse reflectance (DRIFT) accessory. Spectra were collected with a resolution of 8  $\text{cm}^{-1}$  and given as the ratio of 200 single beam scans to the same number of background scans in pure KBr. The original samples were diluted in KBr (2% w/w) and ground to a fine powder. Samples of “apparent” DS below 2.7 were made up by mixing ethylcellulose (EC7) and cellulose powders in different proportions. These blends were also diluted in KBr by following the procedure outlined above.

Powder was ground to obtain the same grain size of the three products (ethylcellulose, cellulose and KBr). Ethylcellulose and ethylcellulose-cellulose blends were

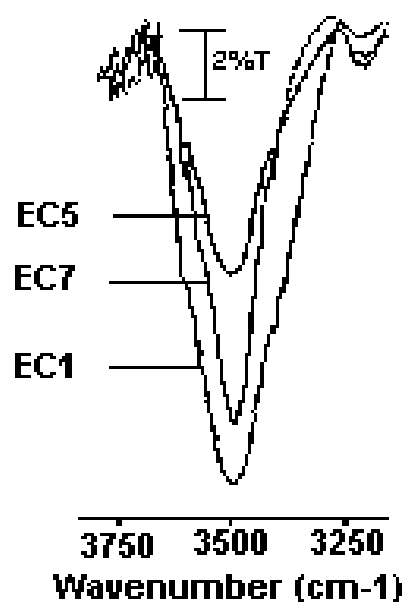


Figure 3. IR spectra of three ethylcellulose samples with different DS in the 3750-3200  $\text{cm}^{-1}$  range.

dried on a thermogravimetric scale and poured onto the DRIFT sample holder before IR spectra acquisition (16-20). The DRIFT holder was filled with the mixture, ensuring the upper surface was as planar as possible by levelling the upper surface. Reproducibility and accuracy of the results was obtained because when spectra were repeated five times, the intensity of the bands were practically the same.

Whenever possible, spectra encompassing the OH stretching band were normalized by dividing the intensity of every spectral single point by the maximum peak intensity of the CH stretching band. This normalization procedure is feasible when comparing spectra of ethylcellulose samples with the same DS, since their maximum CH stretching band intensity is expected to remain constant.

#### Results and Discussion

Figure 2a shows the cellulose infrared spectrum obtained in the 3750-2500  $\text{cm}^{-1}$  range. In this region, two broad bands are obtained. The band centred at about 3350  $\text{cm}^{-1}$  is assigned to OH stretching vibration(11,17,21), and the band at around 2900  $\text{cm}^{-1}$  is assigned to CH stretching vibration (21). The IR spectrum for EC7 ethylcellulose (Figure 2b) displays similar vibration features in this frequency region. The rest of the ethylcellulose products behaved similarly.

To check for the influence of DS in the IR spectra,

Table 3. Integrated intensity for bands I and II as calculated from deconvoluted spectra of ethylcellulose-cellulose blends.

Sample	DS	Band I	Band II	$I_{II}/I_I$
		$I / \text{a.u.}$	$I / \text{a.u.}$	
EC7	3	8.28	0.20	0.02
F	2.9	8.07	0.42	0.05
E	2.7	10.22	0.89	0.09
D	2.4	9.43	3.71	0.39
C	1.8	10.77	12.12	1.12
B	1.2	12.02	18.19	1.51
A	0.6	11.41	30.05	3.63
Cellulose	0	17.73	39.72	-

the following three products were studied: EC7 (DS=3.0), EC5 (DS=2.9) and EC1 (DS=2.7). Figure 3 shows their corresponding IR spectra in the region of 3750-3200  $\text{cm}^{-1}$ . A small widening of the OH stretching band and a sharp increase in band intensity is observed as DS decreases.

In order to confirm these trends, ethylcellulose samples with lower DS would be required, but they are unfortunately not commercially available. This problem may be overcome by studying the spectral features of different mixtures of ethylcellulose-cellulose in powder form, in order to obtain samples with "apparent" DS covering a wide range below 2.7. The DS values for some of the blends employed in this study (EC7-cellulose blends) are shown in Table 3.

The IR spectra for EC7-cellulose blends in the region of 3750-3200  $\text{cm}^{-1}$  are superimposed in Figure 4, together with those for pure EC7 and pure cellulose. These spectra show a band centred at about 3500  $\text{cm}^{-1}$  (hereafter referred to as band I) and a band at low wavenumber (hereafter named band II) that develops and overlaps with the former as DS decreases. As discussed above, band I is ascribed to OH bound to C1 and C4 positions in end rings. Band II, located at about 3300  $\text{cm}^{-1}$ , can be assigned to the stretching vibration of OH groups at C2, C3 and C6 ring positions. This assignment explains the growth of band II with decreasing DS, as a reduced number of ether bonds per ring imply an increased number of OH groups at C2, C3 and C6 positions.

The preceding observations were quantified by

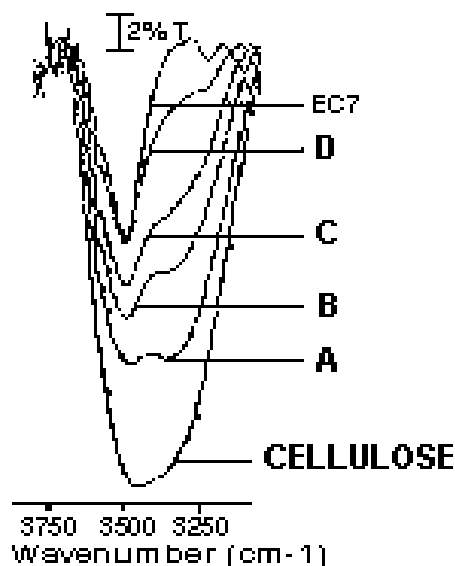


Figure 4. Cellulose/ethylcellulose blends infrared spectra. "Cellulose" DS=0, "A" DS=0.6, "B" DS=1.2, "C" DS=1.8, "D" DS=2.4, "EC7" DS=3.

deconvoluting the various OH stretching vibration contributions in Figure 4. The measured envelope was regarded as the convolution of peaks with Gaussian line shapes. The best fits were obtained with only two Gaussian peaks with maximums at wavenumber 3500  $\text{cm}^{-1}$  for band I, and 3300  $\text{cm}^{-1}$  for band II). Deconvolution results for representative spectra are shown in figure 5. A very good agreement between the experimental vibration envelope (dotted line) and the fitting curve (solid line) is observed, calculated by convoluting the two individual contributions (dashed line). The integrated intensity of the two deconvoluted bands is also tabulated in Table 3 for the different blends, as well as the integrated intensity ratio  $I_{II}/I_I$ .

Inspection of the integrated intensities in Table 3 reveals that band I remains constant in a broad range of DS (see figure 6). This behaviour is fully consistent with our previous assignment to OH vibrations at C1 and C4 positions in terminal rings, which should not be affected by ethyl ether substituents. On the other hand, the integrated intensity of band II rises appreciably as DS diminishes, which also reinforces our suggestion that this band is related to OH bound at C2, C3 and C6 positions along the polymeric chains. Finally, it should be noted that the evolution of the integrated intensity ratio  $I_{II}/I_I$  parallels that of the band related to the population of substitutable OH groups (see Table 3). Thus, the estimation of this ratio from IR measurements could be helpful in the evaluation of the DS of ethylcellulose

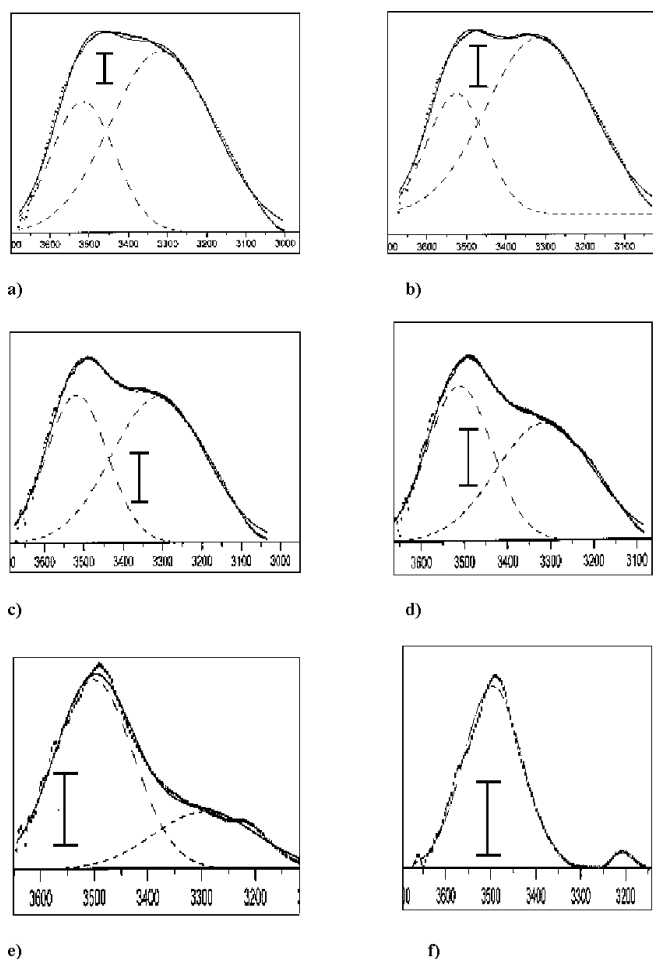


Figure 5. Deconvolution of the OH stretching band of significant cellulose/ethylcellulose blends. "a" DS=0, "b" DS=0.6, "c" DS=1.2, "d" DS=1.8, "e" DS=2.4, "f" DS=3. Segment shows 0.02% of absorbance for each figure, and x axis indicates wavenumbers ( $\text{cm}^{-1}$ ). (.....) Experimental values, (- - -) Deconvoluted Bands, (—) Sum of deconvoluted bands.

samples.

The behaviour of IR measurements on ethylcellulose with DS = 2.9 and DS = 2.7 was compared with ethylcellulose – cellulose blends; the results of this are shown in table 4. When  $I_{II}/I_I$  ratio is studied, a good correlation was achieved between ethylcellulose samples and those with the same "apparent" DS values (EC7 cellulose blends).

The application of all these findings to the discussion of the spectral results of real ethylcellulose samples of different DS (Figure 3) allows one to conclude that the observed enlargement of the OH bandwidth at DS<3 is due to the development of band II. According to the results displayed in Figure 4, the weight of band II in the maximum height of the OH band envelope is only

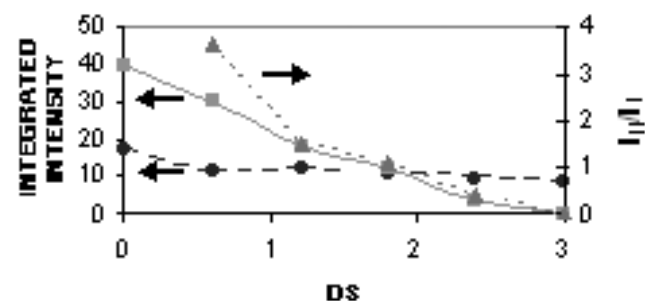


Figure 6.- Integrated intensities of Band I and Band II for different DS obtained from the deconvolution of the IR spectra of cellulose/ethylcellulose blends. (- - ● - -) Band I, (—■—) Band II, (●●●●●)  $I_{II}/I_I$ .

Table 4. Comparison of intensity for bands I and II between commercial and diluted samples.

Sample	DS	$I_{II}/I_I$
EC7	3	0.02
EC5	2.9	0.05
EC4	2.9	0.05
EC3	2.9	0.05
EC2	2.9	0.05
F	2.9	0.05
EC1	2.7	0.09
E	2.7	0.09

significant at apparent DS below 2.4. Thus, the different heights shown in Figure 3 are most likely due to the inability to normalize the three spectra, rather than a true increase in intensity.

As stated above, the bands centred at about  $3500 \text{ cm}^{-1}$  correspond to the OH stretching vibration (17,21). Kondo *et al.* (11) assigned this band to OH groups bound to C1 and C4 carbons in terminal anhydroglucose rings (see figure 1). These hydroxyl groups are involved in the formation of glycosidic ether bonds and hence their population should vary within chain length modifications, i.e. with DP changes. Nevertheless, no significant variations are observed within the ethylcellulose family studied in the spectral region of  $3750\text{-}3200 \text{ cm}^{-1}$ . The same observation is made in the ethylcellulose family with DS=3. These results suggest that the DP variations in both series involve OH population changes at chain ends,

which are not sufficiently important to show discernable modifications in the IR band intensity. This indicates that IR measurements are not suitable for checking structural changes derived from DP variations in ethylcellulose samples, at least in the range of DP values studied in the present work.

## Conclusions

Infrared spectra of all ethylcellulose samples studied displayed several characteristic vibration properties in the region of between 3750 and 2500  $\text{cm}^{-1}$ , a sharp band at 2900  $\text{cm}^{-1}$ , associated with a CH stretching vibration, and a broader band at higher wavenumber, which corresponds to OH stretching modes. A careful analysis of several ethylcellulose-cellulose blends at different positions show that this latter band is indeed comprised of two different components centred at 3500  $\text{cm}^{-1}$  (band I) and 3300  $\text{cm}^{-1}$  (band II), respectively. The integrated intensity of band I is insensitive to the DS of the ethylcellulose chain and may be attributed to the stretching vibration of hydroxyl groups bonded to C1 and C4 positions of terminal anhydroglucose rings. The integrated intensity of band II increases greatly with decreasing DS, as expected for a vibration band related to non-substituted OH groups at C2, C3 and C6 ring positions within the entire polymeric chain, and a noticeable widening of the band envelope ensues.

As far as DP is concerned, its effect on the OH stretching band is negligible, at least in the range of DP values studied in this work. IR spectroscopy proved to be a suitable tool in checking ethylcellulose structural changes related to DS variations, but it has not been able to detect DP changes.

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