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# Mercerized linters cellulose: characterization and acetylation in *N*,*N*-dimethylacetamide/lithium chloride

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## Abstract

Linters cellulose was subjected to different treatments (mercerization and ionized air) before acetylation with acetic anhydride, in homogeneous medium, using DMAc/LiCl as solvent system. Before derivatization, the treated fibres were characterized by Scanning Electron Microscopy, X-ray diffraction, alpha-cellulose content, Inverse Gas Chromatography and viscosimetry. It was shown that except a decrease in the dispersive surface energy, the treatments induced small changes in the cellulose. The degree of acetylation of these fibers was found to follow a linear behavior with the stoichiometry between acetic anhydride and glucose unit, but this linearity obeyed high rate up to a DS of 2.0. The order of reactivity observed for all samples, C6 > > C2 > C3, confirms the higher reactivity of OH in C6 position, because this group is the least sterically hindered of the anhydroglucose unity.

*Keywords:* Iinters cellulose; Cellulose acetate; Inverse gas chromatography (IGC); Cellulose surface energy; DMAc/LiCl

## 1. Introduction

The task of dissolving native, unsubstituted cellulose without its chemical changes is extremely difficult on account of the rigidity of this macromolecule and the very stable parallel structure into which the chains are packed, both these characteristics being the result of numerous cooperating intra- and intermolecular hydrogen bonds (Hattori, Cuculo, & Hudson, 2002). Cellulose dissolution has been studied extensively and a variety of solvent systems is known (Morgenstern and Kammer, 1999), the DMAc/LiCl system, first described by McCormick and Lichatowich (1979), being the most frequently used (El-Kafrawy, 1982; Dawsey and McCormick, 1990; Bianchi, Marsano, Ricco, & Conio, 1997; Spange, Reuter, Vilsmeier, Heinze, Keutel, & Linert, 1998; Marson and El Seoud, 1999; Ass and Frollini, 2001; Heinze and Liebert, 2001; Potthast, Rosenau, Sixta, & Kosma, 2002; Potthast, Rosenau, Sartori, Sixta, & Kosma, 2003).

Generally, the solubility of cellulose depends strongly on its molecular weight and the degree of crystallinity (Hattori et al., 2002) and it is necessary to explore separately the conditions of solubility for cellulosic material from each source (Isogai and Atalla, 1998). In fact, different celluloses exhibit differences with respect to solubilization and aggregation (irreversible) and/or association (reversible) of their polymer chains that may occur in solution. Such variations may influence the degree of substitution of a derivative whose synthesis involves the dissolution of cellulose first, such a way that the derivative is prepared in homogeneous medium. Thus, each type of cellulose must be studied in detail to discover the most suitable conditions, in order to maximize its solubility and optimize the synthesis of products.

For instance, the cellulose from cotton linters used in this study is very pure, with a high degree of crystalline order, so that the polymer chains are closely packed and do not dissolve in DMAc/LiCl, unless the linters is first mercerized with alkaline solution, as described later. This treatment is not necessary for all types of celluloses. For example, when the cellulose from sisal is extracted from the plant fiber, it often contains a certain proportion of hemicelluloses, and the mixed chains are not packed so neatly in the solid

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material. As a consequence, the latter dissolves readily in this medium, even without mercerization pre-treatment (Ciacco, Ass, Ramos, & Frollini, 2000; El Seoud, Regiani, & Frollini, 2000). The acetylation of cellulose in DMAc/LiCl was considered by Tosh, Saikia, and Dass (2000), but using different conditions relating to the present work, as for instance pyridine and *p*-toluenesulfonyl chloride as catalysts. Diamantoglou and Kuhne (1988) studied the esterification of cellulose, including acetylation reaction, in the presence of various catalysts. In the present work, it was intended optimize the conditions of linters cellulose acetylation reaction with no catalyst present.

Mercerization alters the fine structure and morphology of the fiber as well as the conformation of the cellulose chains (moving from cellulose I–II), producing changes in the strength and shine of the fiber and in its adsorption properties. During this process, the material swells and the polysaccharide chains are rearranged; the amount of less-ordered material in the fiber rises, while the crystalline part contracts. These changes result in higher adsorption, as mercerization increases the specific surface area of the fiber, making more easily accessible the hydroxyl groups of cellulose macromolecules (Pusic, Grancaric, Soljacic, & Ribitsch, 1999).

In the present study, the linters cellulose was submitted to mercerization, in order to render it soluble in DMAc/LiCl and remove any extraneous material soluble in alkaline medium. The same cellulose was also treated with a combination of mercerization and exposure to an atmosphere of ionized air. Any means of reducing the degree of aggregation of the cellulose chains would be of great benefit in the synthesis of derivatives by heterogeneous reaction of non-dissolved cellulose; it might also permit its dissolution under milder conditions (reduced times and temperatures) and thus lower the cost of synthesis through homogeneous reaction. Such aggregation, apart from being promoted by the strong cooperative interactions produced by intermolecular hydrogen bonds, may also be enhanced by electrostatic interactions, which might be reduced by the ionized-air treatment.

In view of the possibility that the above treatments could alter the surface energy of the raw material and that this would affect the initial interaction when the polymer and DMAc/LiCl solvent are brought into contact, surface-energy properties of the cellulose were determined by Inverse Gas Chromatography (IGC), which is based on the adsorption of probe vapors with the fiber packed into the column of a gas chromatograph. The principle and experimental details related to IGC have been reported elsewhere (Kazayawoko, Balatinecz, & Romansky, 1997; Belgacem and Gandini, 1999, chap. 2; Gutierrez, Rubio, Rubio, & Oteo, 1999; Planinsek, Trojak, & Srcic, 2001).

As already mentioned, the properties of the linters cellulose have an influence on its solubility in DMAc/LiCl and hence on the properties of the derivatives obtained by modifying the polysaccharide in this medium. Moreover, various reaction conditions should be tested, to discover the best ones for each cellulose-solvent-reagent combination. In the work reported here, linters cellulose, both mercerized and untreated, was investigated in detail, and the conditions of acetylation, such as the time of reaction and molar ratio of the reagent to the anhydroglucose unit, were varied in an attempt to optimize the synthesis of linters cellulose acetate.

This investigation of linters as a raw material forms part of a wider project of research into reactions of cellulose in homogeneous medium, involving celluloses from several plant sources (linters, cotton, sisal and sugarcane bagasse) that grow much more rapidly than trees, from which wood, the main current source of cellulose, is obtained (Regiani, Frollini, Marson, Arantes, & El Seoud, 1999; Ciacco et al., 2000; El Seoud et al., 2000; Marson, Ciacco, Frollini, & El Seoud, 2000; Ass et al., 2001). Each of these types of cellulose has been tested, to find the best conditions for solubilization in DMAc/LiCl and synthesis of derivatives in solution. Such information on the behavior of each type of cellulose in this system can be useful in the future, considering the possibility of development of large-scale processes to produce derivatives of these low-cost celluloses.

## 2. Experimental

### 2.1. Materials

The cellulose used as raw material here was low DP cotton linters (used in textile industry), kindly provided by Indústria Fibra S/A, Americana, SP, Brazil. *N*,*N*-dimethylacetamide (DMAc, VETEC) and acetic anhydride ($Ac_2O$, Mallinckrodt) were dried over 4 Å molecular sieves. Lithium chloride (LiCl, Mallinckrodt) was dried at 90 °C under vacuum and afterwards stored in a desiccator. Synthesis grade methanol and sodium hydroxide were used as received.

### 2.2. Cellulose mercerization

Cellulose from linters was mercerized in 10, 20, 30 and 40% NaOH solution (material: liquor ratio 1:50 w/w) at 0 °C for 1.0 h (Buschle-Diller and Zeronian, 1992). The alkali-swollen material was washed with distilled water until the pH of the filtrates remained unchanged. The mercerized product was air-dried and kept at 60 °C under vacuum, until constant weight.

### 2.3. Treatment of cellulose surface with ionized air

The system used for air ionization was homemade. It consists of a stainless steel box with a lid securing 6 ionization nozzles (HS Nozzle-SIMCO) and a 7.5 kV power supply, connected in a dry air line. Linters cellulose was exposed to a flow of ionized air for 1.0 and 5.0 h.

## 2.4. Characterization of cellulose

### 2.4.1. Degree of polymerization (DP)

This was determined by measuring the viscosity (25 °C) of cellulose solution in Cuen (copper:ethylene diamine, 1:1 v/v), using an Ostwald viscometer. The average molar mass is given by $\overline{\mathrm{Mv}} = \overline{\mathrm{DP}} \times 162$, according to TAPPI standard T230 om-89 (TAPPI, 1990).

### 2.4.2. Crystallinity index (Ic)

It was determined by X-ray diffraction, using a VEB CARL ZEISS-JENA URD-6 Universal Diffractometer operating at 40 kV/20 mA and $\lambda(\mathrm{Cu\ K}\alpha) = 1.5406$ Å. Ic is calculated according the equation $I_c = 1 - I_1/I_2$, where $I_1$ is a minimum intensity and $I_2$ is a maximum intensity (Buschle-Diller et al., 1992).

### 2.4.3. Alpha-cellulose content

This is given by the loss of mass after treatment of cellulose with 17.5% NaOH solution, (25 °C). It is defined as % $\alpha$-cell = (mass of dry $\alpha$-cell/mass of dry cell) × 100 (Browning, 1967).

### 2.4.4. Morphological surface analysis

Cellulose surfaces were examined by Scanning Electron Microscopy (SEM) using a LEO 440 ZEISS/LEICA model. Samples were metalized with gold.

### 2.4.5. Surface energy analysis

In order to estimate the contribution of dispersion (London) forces to the surface free energy of linters cellulose, pretreated in various ways, the samples were analyzed by Inverse Gas Chromatography (IGC). A Shimadzu GC-17A gas chromatograph with a flame ionization detector (FID) was used. The columns used were made from stainless steel (316) and had an internal diameter of 4.0 mm and a length of 1.0 m. The injector and detector were maintained at 100 °C, the column at 50 °C. The carrier gas ($N_2$) flowed at 30 mL/min. Before each test, the columns, packed with the cellulose samples, were conditioned overnight at 110 °C with $N_2$ flowing, to remove traces of water and volatile contaminants. In order to work at infinite dilution conditions, very small amount of the probes were injected. Thus, 10 μL of the vapor probe was injected with a gas-tight Hamilton micro-syringe. The nonpolar probes consisted of the series of *n*-alkanes from pentane to decane (Sigma-Aldrich), with methanol as marker, and each probe was tested in triplicate.

## 2.5. Dissolution and acetylation of linters cellulose

The dissolution and acetylation steps were similar to those used by Edgar, Arnold, Blount, Lawniczak and Lowmann, (1995) with some modifications. A mixture of cellulose (2.00 g) and 100 mL of DMAc (see Table 1) was heated to 150 °C and stirred for 1.0 h, in a glass reactor equipped with a mechanical stirrer and reflux condenser, under a flow of $N_2$. Then, 6.0 g of lithium chloride were added and the reflux condenser was substituted by a short-path distillation apparatus. The mixture was heated to 170 °C and 15% of the solvent volume was distilled off with the aim of eliminating most of the residual water present in both solvent and cellulose. The reaction mixture was then cooled to room temperature and allowed to stir overnight. A clear cellulose solution was obtained and the temperature was raised to 110 °C, under reflux and a flow of $N_2$. Acetic anhydride ($Ac_2O$) was added drop wise, in appropriate molar ratios to the anhydroglucose units (AGU), as given in Table 1. The system was kept at 110 °C for various times, as summarized in Table 1, and then cooled to room temperature. The product was precipitated with methanol and purified by Soxhlet extraction in methanol. Finally, the cellulose derivative was dried at 50 °C under vacuum, until constant weight.

Table 1
Reaction conditions and degree of substitution of cellulose acetates obtained

| Acetate | Cellulose | Acetylation time (h) | Molar ratio $Ac_2O$:AGU | Degree of substitution (DS) |
|---|---|---|---|---|
| 1 | Mercerized in 10% NaOH | | | 1.9 |
| 2 | Mercerized in 20% NaOH | | | 1.9 |
| 3 | Mercerized in 30% NaOH | | | 1.8 |
| 4 | Mercerized in 40% NaOH | 1.0 | | 1.9 |
| 5 | Mercerized in 20% NaOH + exposed for 1.0 h to ionized air | | 3.0 | 1.6 |
| 6 | Mercerized in 20% NaOH + exposed for 5.0 h to ionized air | | | 2.0 |
| 7 | | 2.5 | | 1.9 |
| 8 | | 4.0 | | 1.9 |
| 9 | | 5.5 | | 1.9 |
| 10 | | | 1.5 | 0.6 |
| 11 | | | 2.0 | 1.1 |
| 12 | Mercerized in 20% NaOH | | 2.5 | 1.2 |
| 13 | | 1.0 | 2.8 | 1.3 |
| 14 | | | 3.0 | 1.9 |
| 15 | | | 4.5 | 2.1 |
| 16 | | | 6.0 | 2.2 |

## 2.6. Characterization of cellulose acetates

### 2.6.1. Degree of substitution

The degree of substitution (DS) of cellulose acetates was determined by proton NMR. Spectra were recorded in a Brucker AC-200 spectrometer running at 200 MHz and 80 °C; the number of scans was 392. Samples were dissolved in DMSO-$d_6$ (10 mg/mL). A drop of trifluoroacetic acid was added to the sample solution in order to shift the signal of residual water and hydroxyl protons to a lower field, outside the spectral region of interest, without affecting the chemical shifts of the glucose ring protons (Edgar et al., 1995).

### 2.6.2. *Distribution of acetate groups in the anhydroglucose unit (AGU)*

$^{13}$C NMR spectra were recorded using a Brucker AC-200 spectrometer working at 50 MHz, in DMSO-$d_6$ (50 mg/mL, 80 °C, 8000 scans). To ensure fast relaxation of the carbonyl carbon atom of the acetyl group, a solution of 20 mg of Cr(III) in 0.5 mL of acetylacetonate was added. The data were recorded overnight, using the INVGATE (inverse gatted decoupling) program.

### 2.6.3. *Molar mass and distribution of molar mass*

The average molar mass was determined by size exclusion chromatography (SEC) using a Shimadzu SCL-10A system controller connected to a LC-10AD pump, CTO 10 column oven and equipped with RID-6A refractive index detector. The column system consisted of a 5 μm mixed PLgel [preceded by a 10 μm (50×7.5 mm) PLgel guard column] with *N*-methyl-2-pyrrolidinone (NMP) (Aldrich HPLC grade) as the mobile phase, flowing at 0.60 mL per min at 60 °C. The system was calibrated with a standard of pullulan molecules of the following molar masses: $1.60\times10^6$, $3.80\times10^5$, $2.12\times10^5$, $1.00\times10^5$, $4.80\times10^4$, $2.37\times10^4$, $1.22\times10^4$ and $5.80\times10^3$ g/mol. Before being injected into the SEC system, the cellulose acetate solution in NMP was filtered through a 0.45 μm PTFE membrane filter. The acetate injected cellulose acetate solutions had a concentration of 0.0040 g/mL NMP.

### 2.6.4. *Solubility*

The solubility of cellulose acetates at room temperature was cheeked in the following solvents: *N*,*N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP), pyridine and water, considering a concentration of 0.01 g/mL solvent.

## 3. Results and discussion

### 3.1. *Characterization of cellulose*

The scanning electron micrographs presented in Figs. 1–4 show surfaces of mercerized using different treatment conditions and virgin cellulose linters.

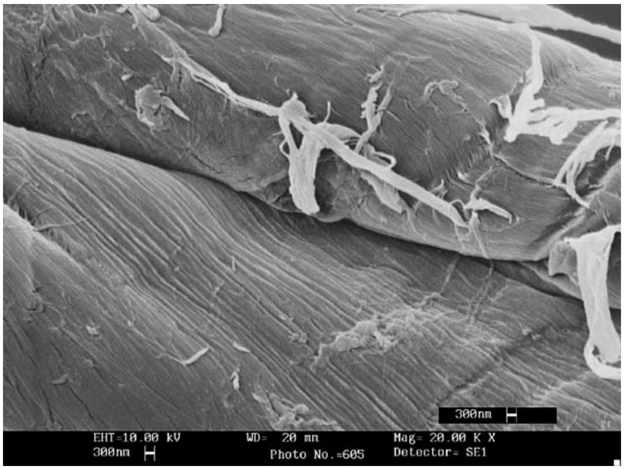

Fig. 1. SEM micrograph of untreated linters cellulose (×20,000).

The surface of mercerized linters (Figs. 2 and 3) is smoother than that of untreated linters (Fig. 1), which indicates that there are no fragments stuck to the fibers, suggesting that some fragments have been eliminated during the mercerization procedure. The effect of increasing NaOH concentration (Figs. 2–3 illustrating the effect of increasing NaOH from 20 to 40%) was also studied and showed that the fibers bundles are loosened, moving then slightly apart. If one compares the sample mercerized in 20% NaOH (Fig. 2) with the same material after 5.0 h of exposure to ionized air (Fig. 4), it can be observed that this treatment promoted an additional separation of the fibers bundles.

During the treatments, cellulose chains can be degraded by the hydrolysis of the glycosidic bonds, resulting in a reduced degree of polymerization. This hypothesis was not observed in our case, since even at the highest concentrations of NaOH (30 and 40%), this degradation was very mild (DP = 407 and 405, respectively), as summarized in Table 2, which presents the data obtained from the characterization of cellulose. This could be attributed to the mild conditions used in this study, namely: low temperature (0 °C) and short treatment time (1.0 h) of the mercerization.

The ionized-air treatment may lead to the removal of contaminants from the fiber surface, normally low molar mass degradation products (Belgacem, Czeremuszkin, Sapieha, & Gandini, 1995). In the present work, the molar mass of the cellulose changed little during this treatment, compared to the mercerized control, indicating that under these conditions practically no damage occurred. In fact,

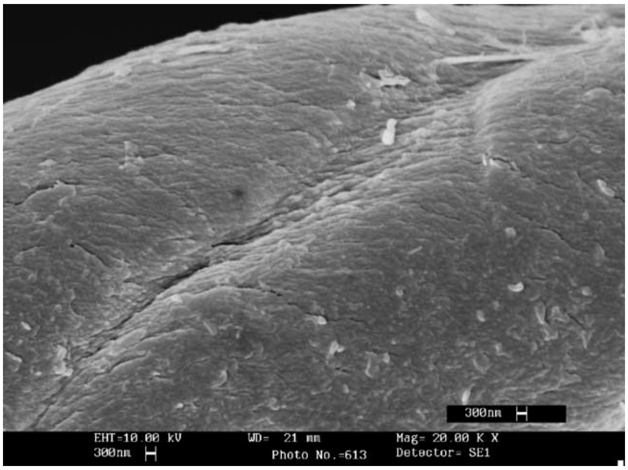

Fig. 2. SEM micrograph of 20% NaOH mercerized linters (×20,000).

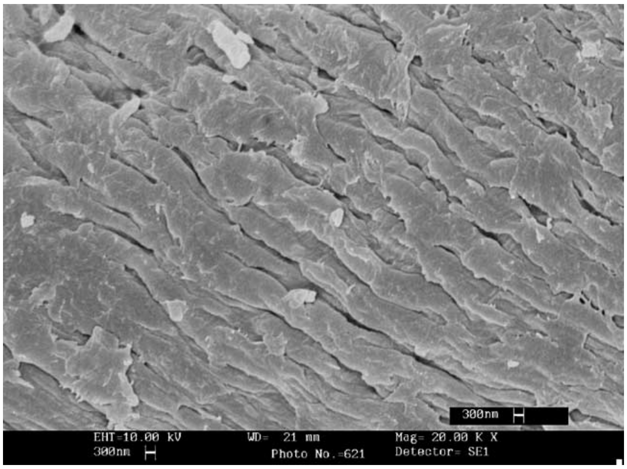

Fig. 3. SEM micrograph of 40% NaOH mercerized linters (×20,000).

mercerization and exposure to ionized air caused very little damage to the cellulose with regard to its molar mass and they may be considered suitable preparatory treatments within the conditions used.

X-ray diffraction patterns of mercerized (40% NaOH) and untreated linters are shown in Fig. 5. The crystallinity index ($I_C$) was calculated from the ratio of maximum and minimum intensities in the diffractogram, using the Buschle-Diller-Zeronian equation, which is normally used to compare changes on cotton crystallinite due to treatments the fiber is submitted (Buschle-Diller et al., 1992):

$$I_c = 1 - I_1/I_2. \quad (1)$$

where $I_1$ is a minimum intensity, proportional to the amorphous fraction of the cellulose (at $18° \leq 2\theta \leq 19°$ for cellulose I and $13° \leq 2\theta \leq 15°$ for cellulose II), and $I_2$ a peak intensity, in which the signal from the crystalline fraction is included (at $22° \leq 2\theta \leq 23°$ for cellulose I and $18° \leq 2\theta \leq 22°$ for cellulose II).

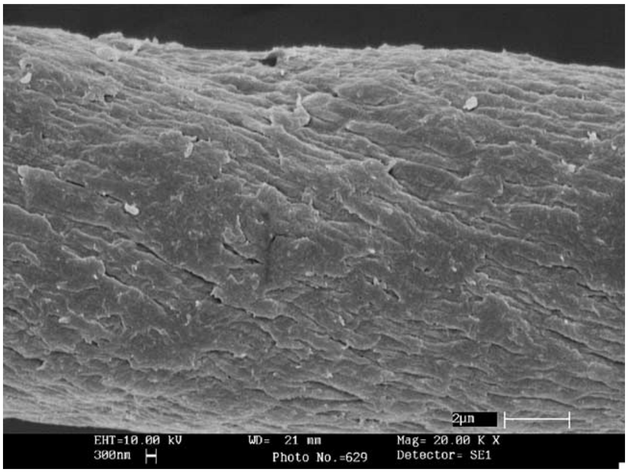

Fig. 4. SEM micrograph of 20% NaOH mercerized linters exposed to ionized air for 5.0 h (×20,000).

Table 2
Degree of polymerization (DP), crystallinity index ($I_c$) and alpha-cellulose content (α-cell) of untreated and treated linters celluloses

| Cellulose | DP | $I_c$ (%) | α-cell (%) |
|---|---|---|---|
| Linters | 414 | 79 | 92 |
| 10% NaOH mercerized linters | 414 | 67 | 93 |
| 20% NaOH mercerized linters | 408 | 72 | 94 |
| 30% NaOH mercerized linters | 407 | 69 | 94 |
| 40% NaOH mercerized linters | 405 | 69 | 93 |
| 20% NaOH mercerized linters and submitted to ionized air for 1.0 h | 410 | 73 | 94 |
| 20% NaOH mercerized linters and submitted to ionized air for 5.0 h | 406 | 67 | 93 |

During mercerization, the alkali penetrates the cellulose fiber and causes a rearrangement of the crystal packing of chains from native cellulose I (chains aligned in parallel) to cellulose II (anti-parallel). This change is irreversible and normally accompanied by a decrease in the crystallinity (Nishimura and Sarko, 1987; Buschle-Diller et al., 1992). Treatment with 20% NaOH reduced the value of $I_C$ by 7% (Table 2) and, when the resulting mercerized sample was exposed to ionized air for 5.0 h, $I_C$ fell by a further 5%.

The NaOH treatment probably loosens the bonding within the fiber bundles, causing the fibers to move apart and let the ionized air penetrate further and reach the interior crystalline zones, where it provokes the observed changes. It should be stressed that raw linters cellulose, even after exposure to ionized air, remains insoluble in DMAc/LiCl in the conditions described here.

The α-cellulose content represents the purity of the cellulose, being the non-degraded high molar mass fraction that remains, free of hemicellulose, mineral salts or other contaminants, when the native cellulose is extracted with 17.5% NaOH (TAPPI, 1988). Since cotton linters consisted almost entirely of pure cellulose (Fengel and Wegener, 1989; Kimura and Kondo, 2002), no significant change was observed in the α-cellulose content when the samples were mercerized, nor when exposed to ionized air. Nevertheless, the removal of 1–2% of impurities (see Table 2) may be

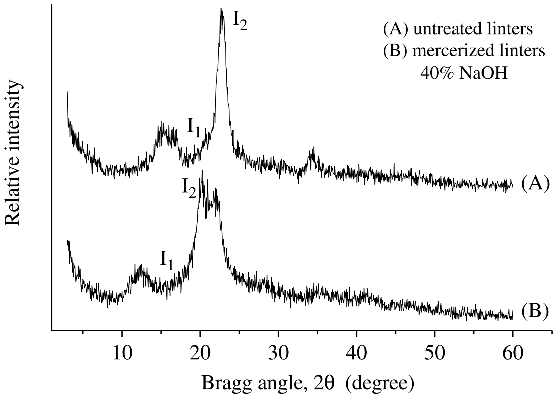

Fig. 5. X-ray diffraction patterns of linters: (A) untreated; (B) mercerized in 40% NaOH.

important, as these alkali-soluble substances could influence the solubilization of cellulose in certain solvents, such as DMAc/LiCl.

The dispersive component of the surface free energy was calculated according to Schultz' approach (Schultz and Lavielle, 1989, chap. 14), and applying the 'zero coverage approach'. In the IGC experiments, the time each *n*-alkane probe retained on the GC column is recorded. From this retention time, $t_R$, and that of the marker, to, the net retention volume, $V_n$, is given by:

$$V_n = \mathrm{JD}(t_R - t_o) \tag{2}$$

where *J* is the flow-rate of the carrier gas and D is a correction factor of the gas compressibility.

Then, the following thermodynamic relation can be used to determine the London component of the surface free energy of the cellulose ($\gamma_S^D$):

$$RT \ln Vn = 2N(\gamma_S^D)^{1/2} a (\gamma_L^D)^{1/2}. \tag{3}$$

where *N* is Avogadro's number, *a* the surface area of the probe molecule, $\gamma_L^D$ the dispersive component of the surface free energy of the probe in the liquid state, *R* the gas constant (8.314 J $K^{-1}$ $mol^{-1}$) and *T* the absolute temperature of the column.

Plotting RT ln $V_n$ against a $(\gamma_L^D)^{1/2}$ gave a straight line, known as the reference line (Belgacem at al., 1995; Tshabalala, 1997). Fig. 6 shows such a line, taken as an example and constructed for a column packed with linters mercerized in 20% NaOH and exposed to ionized air for 5.0 hours. Similar plots were obtained for the other samples of cellulose.

The histogram in Fig. 7 displays the values of $\gamma_S^D$ obtained with various mercerized and untreated linters packed into GC columns, to show the variation of $\gamma_S^D$ with concentration of NaOH used in the treatment.

The value of $\gamma_S^D$ in the untreated linters (29 $mJm^{-2}$) is close to those in the literature (Belgacem et al., 1995; Belgacem et al., 1999) for celluloses extracted from other plant sources (around 30 $mJm^{-2}$). It can be seen in the histogram that $\gamma_S^D$ decreases after NaOH treatment, but there is no clear correlations between the extent of this change and NaOH concentration.

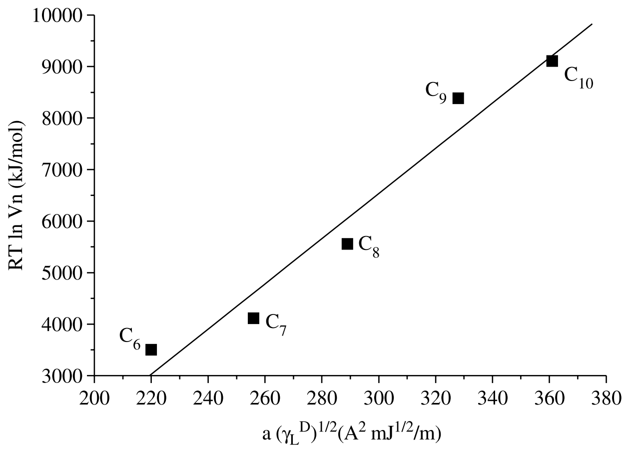

Fig. 6. *N*-alkane reference line for GC column packed with linters mercerized (20% NaOH) and exposed to ionized air for (5.0 h); gradient $\gamma_S^D = 12$ mJ $m^{-2}$.

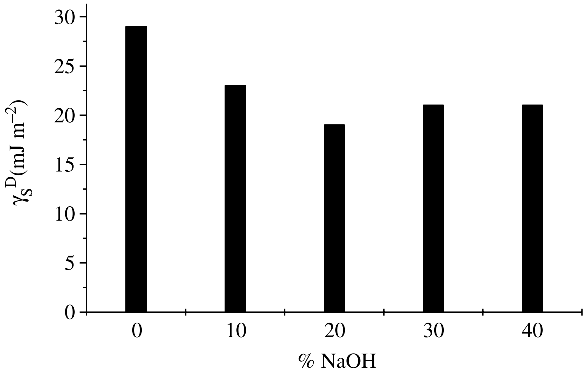

Fig. 7. $\gamma_S^D$ of linters cellulose samples treated with 0–40% NaOH solution.

Linters have a very high α-cellulose content, as already mentioned, and therefore the fraction of non-cellulose material removed by mercerization is small (Table 2), in contrast to what is found in cellulose from other sources, which may exhibit large changes in $\gamma_S^D$ after mercerization (Belgacem et al., 1995; Belgacem et al., 1999).

The sample treated with 20% NaOH, when subsequently exposed to ionized air for 5.0 h, exhibited a decrease in $\gamma_S^D$ from 19 (Fig. 7) to 12 $mJm^{-2}$ (Fig. 6). It should be recalled that ionized-air treatment alters the degree of aggregation of the fiber bundles, and this may affect their interaction with nonpolar probes and, hence, with $\gamma_S^D$. Moreover, the decrease of the crystallinity observed for all treated samples, led to a decrease of $\gamma_S^D$, as reported previously to support the difference in the dispersive surface energy between cellulose and starch (Belgacem, Blayo, & Gandini, 1996). These values seem to be weak, but it is worth noting that they were obtained at 50 °C. If one extrapolates the values of $\gamma_S^D$ to room temperatures they will increase significantly, since the $-d\gamma_S^D/dT$ is about 0.3 mJ $m^{-2}$ (Belgacem et al., 1995; Belgacem et al., 1999).

The stronger the interaction between the sample and a volatile probe, the greater will be the slope $\gamma_S^D$ of the reference line (Fig. 6), the liquid retention volume $V_n$ (Eq. (2)) and the column retention time $t_R$ (Eq. (2)). Therefore, when a treatment reduces $(\gamma_S^D)^{1/2}$, this implies that it reduces the number of non-polar sites on the fiber, enhancing its polar character. In the present case, in addition to altering the packing of cellulose chains, mercerization removes waxy material (small non-polar molecules) and thus should leave the surface richer in pure cellulose, with polar hydroxyl groups in a more exposed conformation. This hypothesis is supported by the observed lowering of $\gamma_S^D$ after mercerization. The same can be said of the ionized-air treatment, which further separates the fibers and so must expose more internal hydroxyl groups, reducing $\gamma_S^D$, as seen in Fig. 6.

The importance of determining the components of surface free energy of a solid sample lies in the fact that changes in these parameters may indicate concomitant changes in surface interactions with other material. The latter might be another solid phase, as when cellulose fibers are used to reinforce polymer-matrix composites, or a liquid, as at the start of solubilization of cellulose in a solvent system. Thus, in the present case, apart from the intrinsic interest in knowing the effects on $\gamma_S^D$ of the various treatments applied to the linters, there was also the aim of discovering whether a relation exists between $\gamma_S^D$ and the readiness of cellulose to dissolve in DMAc/LiCl. The experiments in fact revealed a significant difference between the values of $\gamma_S^D$ in raw (insoluble) and mercerized (soluble) cellulose; furthermore, just as the NaOH concentration used did not correlate significantly with $\gamma_S^D$, among the diverse mercerized samples, so their readiness to dissolve in DMAc/LiCl was independent of this concentration.

### 3.2. Characterization of cellulose acetates

The DS values of the cellulose acetates were calculated by means of the ratio between the area corresponding to the proton resonance of the glucose ring ($\delta \sim 2.60$–$5.20$ ppm) and the corresponding resonance area of the methyl protons of the acetate group ($\delta \sim 1.80$–$2.20$ ppm) (Edgar et al., 1995), as shown in Fig. 8. Table 1 presents the DS values of the cellulose acetates.

The distribution of the acetyl moiety at primary (C6-OH) and secondary (C2-OH and C3-OH) groups of the AGU was calculated from $^{13}$C NMR spectra (Kamide and Okajima, 1981) (Table 3). The order of reactivity observed for all samples, $C6 \gg C2 > C3$, confirms the higher reactivity of OH in C6 position, because this group is the least sterically hindered of the AGU unity (Marson et al., 1999). The lower reactivity of C3-OH when compared with C2-OH can be related to the fact that the first hydroxyl group can be still involved in intramolecular hydrogen bond. As is well-known, there is one intramolecular hydrogen bond between the OH at C3 position and the heterocyclic oxygen atom of the neighboring unit of celluloses dissolved in DMAc/LiCl (Nardini and Vincendon, 1986). The relative reactivity of C3-OH with respect to C2-OH seems to indicate that part of C3 groups maintained the intramolecular hydrogen bonds in the homogeneous solution, as already observed by other authors (Marson et al., 1999; Kondo, 1998). The partial DS values of the less substituted acetate (samples 10, 11, 12 and 13, Table 3) confirm the preference of the reactant towards C6-OH. When near a sixth part (sample 10, Table 3) or third part (samples 11, 12 and 13, Table 3) from the available hydroxyls groups are substituted, the C6 position is responsible for around 70% of the substitution.

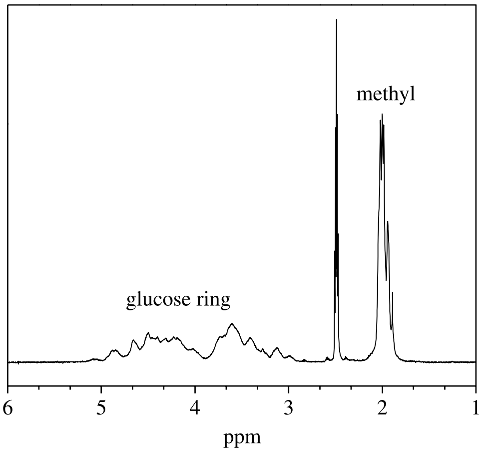

Fig. 8. $^1$H NMR spectrum in DMSO-$d_6$ of cellulose acetate.

Table 3
Partial percentage of acetate group substitution as determined by $^{13}$C NMR

| Sample[a] | % C-6 | % C-2 | % C-3 |
|---|---|---|---|
| 1 | 55 | 25 | 20 |
| 2 | 57 | 27 | 16 |
| 3 | 59 | 24 | 17 |
| 4 | 56 | 27 | 17 |
| 5 | 60 | 26 | 14 |
| 6 | 54 | 32 | 14 |
| 7 | 54 | 24 | 22 |
| 8 | 55 | 27 | 18 |
| 9 | 53 | 28 | 19 |
| 10 | 74 | 15 | 11 |
| 11 | 62 | 21 | 17 |
| 12 | 66 | 18 | 16 |
| 13 | 65 | 19 | 16 |
| 14 | 57 | 27 | 16 |
| 15 | 55 | 28 | 17 |
| 16 | 53 | 31 | 16 |

[a] See Table 1.

Even when a solution of cellulose appears visually homogeneous, there may be a degree of aggregation and/or association of the dissolved polymer chains at a colloidal level. In this case the cellulose molecules are not in 'true' solution and it may not be possible to achieve a very uniform acetylation. Notwithstanding this, homogeneous conditions are still preferable, as the distribution of the substituents along the chains will normally be more uniform than in a heterogeneous reaction. It is important to find the pretreatment and dissolution conditions that maximize the dispersion of the molecules in solution, moreover because the phenomena of aggregation and association may be responsible for the failure to attain stoichiometric acetylation, in terms of the molar ratio $Ac_2O$:AGU, since the hydroxyl groups that form H-bonds between chains will be much less available to react with $Ac_2O$.

The concentration of NaOH used for mercerization was varied over the range 10–40%, with the aim of evaluating its effect on the separation of cellulose fibers in the bundles, which in turn might influence the solubility in DMAc/LiCl and thus the amount of aggregation and the DS of the acetates synthesized. The working hypothesis before this experiment was that a higher concentration of alkali would lead to greater penetration between the polysaccharide chains, increasing their separation and reducing their packing efficiency, thereby facilitating dissolution of the cellulose in DMAc/LiCl and promoting a lower degree of aggregation in solution, which would probably be reflected in higher DS values and more uniform acetylation, as higher amount of hydroxyl groups would be available for reaction.

However, the experimental results of mercerization at 0 °C, presented in Table 1, show that while raising the strength of the alkaline solution does lead to the separation of fiber bundles, allowing fibers to move further apart (see micrograph in Fig. 1 and compare with those of Fig. 3), it has no effect on cellulose solubility and, consequently, none on the acetylation step that follows; i.e., DS values of acetates derived from cellulose samples mercerized at different NaOH concentrations are virtually identical (Table 1).

Continuing the search for pretreatments that might improve the solubilization of linters cellulose, samples already mercerized in 20% NaOH were exposed to a flow of ionized air (1.0 and 5.0 h). This was done because in a parallel research project the same process was tested on bundles of lignocellulosic fibers, which were largely dismantled by this treatment, allowing much better penetration by a polymer resin used to prepare composites reinforced with vegetal fibers (Frollini, Paiva, Trindade, Razera, & Tita, 2004). When samples of linters were pretreated only with ionized air, they remained insoluble in DMAc/LiCl, as mentioned above, and thus could not be acetylated. Therefore, only mercerized cellulose was used in these tests.

It was considered likely that ionized air would neutralize charges on the cellulose surface and causes the fibers to disaggregate, allowing solvent to penetrate and dissolve them more easily. Moreover, it was hoped that as the treated cellulose dissolved, the fibers would be separated and then dismantled into chains dispersed in the solvent, enhancing acetylation and favoring a higher DS in the acetate produced. Examining Table 1 and comparing acetates 5 and 6, made from cellulose mercerized in 20% NaOH and then exposed to ionized air for 1.0 h and 5.0 h respectively, with acetate 2 (mercerized control), it can be seen that after 1.0 h of ionized air the DS decreased from 1.9 to 1.6, while 5.0 h left it practically unchanged. It should be noted that in a parallel research project, a similar result was obtained when sisal cellulose was exposed to ionized air for short periods (Ciacco, 2003).

We have seen that the conditions during both mercerization and exposure to ionized air were varied, with the aim of optimizing first the dismantling of the fibers and then, during solubilization, the dissociation of cellulose molecules on contact with DMAc/LiCl. In fact, both treatments led to changes in the London component of the surface energy (see Figs. 6 and 7 and discussion above) and the crystallinity index (Table 2), and loosened the fiber bundles (Figs. 1 and 3), but they did not lead to further dissociation of the polysaccharide chains in solution, judging by the apparent DS values of acetates synthesized after various pretreatments.

The experiments discussed below were then carried out in an attempt to find the best reaction conditions for the synthesis of cellulose acetates from linters, the target being the stoichiometric DS of 3.0 substituents per AGU. The cellulose used in all these experiments had been mercerized in 20% NaOH. It should be stressed that many of the reactions were carried out in duplicate in order to check the results reproducibility. The relative error was always very small (around 4%), indicating good reproducibility of the results obtained.

The time of acetylation was increased stepwise from 1.0 to 5.5 h, but the DS remained near 1.9 for each of the 4 reaction times, as shown in Table 1 (acetates 2, 7, 8 and 9). Therefore, the DS attained in acetates produced from linters cannot be altered significantly either by pretreatment of the cellulose or by varying the reaction time.

In view of the importance of stoichiometric control of the reaction, it was decided to investigate the relation between the number of moles of $Ac_2O$ per AGU in the initial solution in DMAc/LiCl and the DS of the acetate produced for a reaction time of 1.0 h. Fig. 9 shows the plot of degree of substitution (DS) *vs* the molar ratio between the acetic anhydride and AGU. From this figure, it can be deduced that for products with DS values from 0.6 to about 1.9 (acetates 10–16), there is an approximately linear relation between DS and the molar ratio of reactants $Ac_2O$:AGU ranging from 1.5 to 3.0.

This correlation can be used to achieve a desired DS in the acetylation of linters cellulose in DMAc/LiCl. Moreover, products with any DS from 0.5 to 2.0 and the acetate groups spread uniformly along the chain can be made in this way; such control over this range would be hard to obtain in the heterogeneous reactions used on the industrial scale.

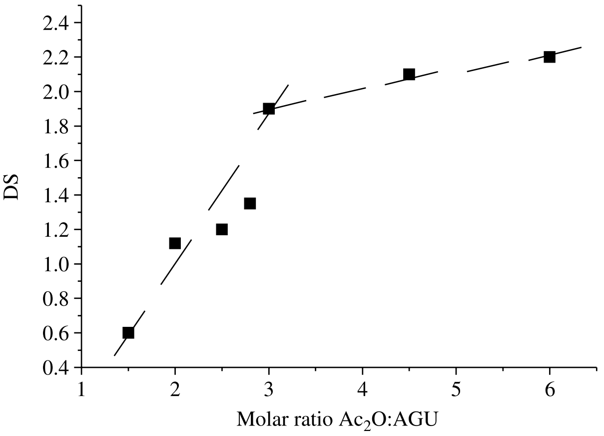

Fig. 9. DS of cellulose acetate as a function of molar ratio of acetic anhydride to AGU. Linters mercerized in 20% NaOH reacted with $Ac_2O$ in DMAc/LiCl solvent for 1.0 h at 110 °C.

Table 4
Molecular weight averages ($M_w$ and $M_n$) and polydispersity index ($M_w/M_n$) for cellulose acetates samples, as obtained from SEC measurements

| Sample[a] | DS | Peak 1 | | | Peak 2 | | |
|---|---|---|---|---|---|---|---|
| | | $M_n$ (g mol$^{-1}$) | $M_w$ (g mol$^{-1}$) | $M_w/M_n$ | $M_n$ (g mol$^{-1}$) | $M_w$ (g mol$^{-1}$) | $M_w/M_n$ |
| 1 | 1.9 | – | – | – | 31000 | 53000 | 1.70 |
| 2 | 1.9 | $1.4\times10^6$ | $1.6\times10^6$ | 1.14 | 32000 | 64000 | 2.00 |
| 3 | 1.8 | $1.2\times10^6$ | $1.3\times10^6$ | 1.10 | 28000 | 51000 | 1.82 |
| 4 | 1.9 | $1.2\times10^6$ | $1.4\times10^6$ | 1.16 | 27000 | 50000 | 1.85 |
| 5 | 1.6 | – | – | – | 23000 | 38000 | 1.65 |
| 6 | 2.0 | – | – | – | 28000 | 64000 | 2.28 |
| 7 | 1.9 | $1.2\times10^6$ | $1.5\times10^6$ | 1.25 | 24000 | 40000 | 1.67 |
| 8 | 1.9 | $1.3\times10^6$ | $1.8\times10^6$ | 1.38 | 24000 | 40000 | 1.67 |
| 9 | 1.9 | $1.0\times10^6$ | $1.3\times10^6$ | 1.30 | 21000 | 34000 | 1.62 |
| 11 | 1.1 | $2.2\times10^6$ | $2.8\times10^6$ | 1.27 | 34000 | 77000 | 2.26 |
| 12 | 1.2 | $1.8\times10^6$ | $2.7\times10^6$ | 1.50 | 23500 | 43000 | 1.83 |
| 13 | 1.3 | $1.9\times10^6$ | $2.4\times10^6$ | 1.26 | 32000 | 61000 | 1.90 |
| 14 | 1.9 | $1.4\times10^6$ | $1.6\times10^6$ | 1.14 | 32000 | 64000 | 2.00 |
| 15 | 2.1 | $1.6\times10^6$ | $2.1\times10^6$ | 1.31 | 30500 | 56500 | 1.85 |
| 16 | 2.2 | $1.6\times10^6$ | $2.2\times10^6$ | 1.37 | 29000 | 55000 | 1.89 |

[a] See Table 1; sample 10 was not soluble in NMP.

When the reagent ratio is above 3.0, yielding acetates with DS exceeding about 2.0, the gradient of the data line in Fig. 9 falls sharply and DS rises very smoothly with additional $Ac_2O$. In any event, when the desired DS is near to 3.0, the heterogeneous reaction is normally adequate, since problems relating to the uniformity of substitution are less severe or even absent when few $-OH$ groups remain.

The fact that the substitution was incomplete under the present conditions, even when a large excess of $Ac_2O$ was used, may indicate that the accessibility of some hydroxyl groups to be attacked by the reagent was hindered by aggregation or association of cellulose chains. Such interactions between the dissolved chains could be intermolecular hydrogen bonds, either present in the original fibers and left intact by the solvent or formed during solubilization in DMAc/LiCl.

Another interpretation could be given and consists on the possible hydrolysis of some ester functions formed, lowering the maximum DS which can be attained, since it is virtually impossible to eliminate all molecules of the water formed during the reaction, especially because of the very hygroscopic character of cellulose and the other components of reaction medium. Evidence that water in the medium can influence the DS of cellulose acetate was obtained in parallel work in these laboratories (Ass, Frollini, & Heinze, 2004), in which linters were acetylated in another solvent system: dimethyl sulfoxide/tetrabutylammonium fluoride trihydrate (DMSO/TBAF.3$H_2O$). Owing to the water of hydration in the salt, a much greater quantity of $Ac_2O$ was needed to reach a DS similar to that obtained in the DMAc/LiCl solvent.

Excepting the acetate with DS 0.6 (sample 10, Table 1), all the samples were soluble in DMAc, DMSO, NMP and pyridine and insoluble in water, at room temperature. Concerning the organic solvents, the acetate with DS 0.6 was only soluble in DMSO, due to its low degree of substitution. However, the last acetate (sample 10, Table 1) swelled in water at room temperature and dissolved in this solvent at 50 °C.

Table 4 shows the data obtained from SEC measurements.

It must be pointed out that no direct relation can be established between the viscosimetric molar masses of the celluloses (the viscosimetry method was used in the present work due to laboratory facilities, Table 2), and those of their acetates, obtained by SEC (Table 4), even accounting for the mass of acetate groups introduced and the DS of each acetate. Apart from the fact that different solvents were used (Cuen for viscometry and NMP for SEC, see experimental part), the SEC data refer to standard molecular markers, here pullulan, and are related to a separation process based on differences in the hydrodynamic volume of the solutes (Sjöholm, Gustafsson, Eiksson, Brown, & Colmsjö, 2000). Then, the average molecular weight of cellulose acetates could only be compared quantitatively with those of cellulose samples analyzed under identical conditions, by SEC.

Excepting samples 1, 5 and 6, all the acetates presented a peak related to very high molecular weight ($\geq 10^6$ g mol$^{-1}$, peak 1, Table 4), as shown for the acetate with DS 1.8 (sample 3, Table 1, Fig. 10). Probably these peaks are related to aggregates that are easily formed both in solutions of polysaccharides (Sjöholm et al., 2000) and those of their derivatives. So, the peak 2 (Table 4) can be considered as representative of the molecularly dispersed cellulose acetates chains. There is no direct correlation between Mn or Mw values and the DS of the acetates (Table 4). The molecular weight values were obtained from SEC measurements, a size exclusion process related to the conformations and then to the hydrodynamics volumes of the chains in the solution. The increase in molecular weight due to the introduction of acetate groups is not necessarily directly

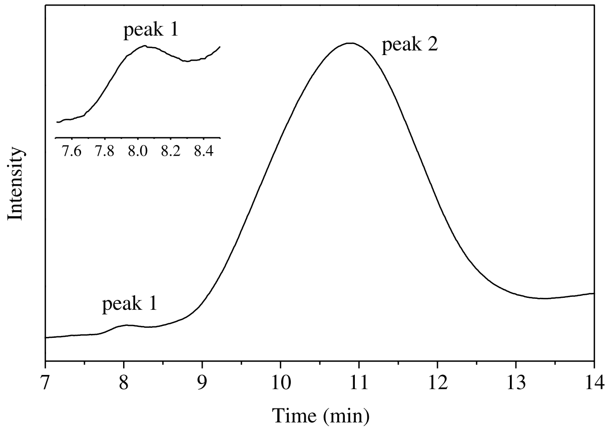

Fig. 10. SEC Chromatogram of cellulose acetate 3 (DS = 1.8).

related to the changes in hydrodynamic volumes which probably become more pronounced with the DS increase. These arguments could explain the absence of correlation between average molecular weight and the degree of substitution.

## 4. Conclusions

Samples of linters cellulose were subjected to mercerization, at various concentrations of NaOH, and also exposed to ionized air for up to 5.0 h. The resulting changes in the properties of the cellulose were analyzed in detail. Apart from the intrinsic interest in studying these changes, it was considered probable that the use of progressively higher concentrations of NaOH and the ionized-air treatment would weaken the aggregation of the bundles of cellulose fibers and subsequently, facilitating the dissolution in DMAc/LiCl, leading then to a gradual reductions in the degree of association and/or aggregation of the cellulose chains. It was then hoped that these changes in the degree of aggregation/association would be reflected in altered DS values of the acetates derived from the treated cellulose. However, this was not observed.

Progressively increasing the reaction time had also practically no effect on the degree of acetylation of the linters cellulose chains in DMAc/LiCl. Furthermore, these DS values were below those calculated from the stoichiometric reaction. Aggregation of cellulose chains in the reaction medium might explain this result, as it leaves fewer hydroxyl groups accessible to the attack by the acetylating agent, but another possible cause is the action of water. Although great care is taken to exclude it from the reaction mixture, the presence of components very hygroscopic makes total elimination extremely difficult. This water may hydrolyze the reagent, acetic anhydride, and/or the ester formed (cellulose acetate), in both cases leading to a lower DS than expected from the stoichiometry used. The relation found between the molar ratio $Ac_2O$:AGU and DS is of value to the industrial chemist, who can use it to calculate the excess of $Ac_2O$ required to produce a given DS.

In conclusion, in this study the acetylation of a cellulose obtained from a rapidly- growing source (cotton linters), in the solvent system DMAc/LiCl, has been thoroughly investigated. It was shown that the reaction can be controlled, with reproducibility, this factor being of fundamental importance for eventual large-scale application.

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