Acetylation of cellulose in LiCl-*N*,*N*-dimethylacetamide: first report on the correlation between the reaction efficiency and the aggregation number of dissolved cellulose

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Abstract The acylation of three cellulose samples by acetic anhydride, Ac₂O, in the solvent system LiCl/ *N*,*N*-dimethylacetamide, DMAc (4 h, 110 °C), has been revisited in order to investigate the dependence of the reaction efficiency on the structural characteristics of cellulose, and its aggregation in solution. The cellulose samples employed included microcrystalline, MCC; mercerized cotton linters, M-cotton, and mercerized sisal, M-sisal. The reaction efficiency expresses the relationship between the degree of substitution, DS, of the ester obtained, and the molar ratio Ac₂O/AGU (anhydroglucose unit of the biopolymer); 100% efficiency means obtaining DS = 3 at $Ac_2O/AGU = 3$. For all celluloses, the dependence of DS on Ac₂O/AGU is described by an exponential decay equation: $DS = DS_o - Ae^{-[(Ac2O/AGU)/B]}$; (A) and (B) are regression coefficients, and DS_o is the calculated maximum degree of substitution,

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Present Address: L. A. Ramos Bahia Specialty Cellulose, Bahia, Brazil achieved under the conditions of each experiment. Values of (B) are clearly dependent on the cellulose employed: $B_{(M-cotton)} > B_{(M-sisal)} > B_{(MCC)}$; they correlate qualitatively with the degree of polymerization of cellulose, and linearly with the aggregation number, N_{agg} , of the dissolved biopolymer, as calculated from static light scattering measurements: (B) = $1.709 + 0.034 N_{agg}$. To our knowledge, this is the first report on the latter correlation; it shows the importance of the physical state of dissolved cellulose, and serves to explain, *in part*, the need to use distinct reaction conditions for MCC and fibrous celluloses, in particular Ac₂O/AGU, time, temperature.

Keywords Cellulose, acetylation of \cdot Cellulose acetate, synthesis of \cdot Cellulose acetylation, efficiency of \cdot LiCl/DMAc \cdot Cellulose solutions, light scattering of

Introduction

This study is part of a research topic that continues to generate much interest, namely, the use of material obtained from renewable sources as a feedstock for the chemical industry. Cellulose is the raw material for several important derivatives, including ethers and esters (Edgar et al. 2001; Rustemeyer 2004; Carollo and Grospietro 2004; Rinaudo and Reguant 2000; Glasser 2004; Edgar 2007; Fischer et al. 2008). It has also been employed in hybrid films with organo-clays (Jan et al. 2009), as reinforcer for starch (Liu et al. 2010), and thermoplastic matrices (Cheng et al. 2007; Ganster and Fink 2006), as well as to prepare different types of cellulose-based nano-composites (Soykeabkaew et al. 2009) and nanoparticles (Heinze and Hornig 2009).

Industrially, cellulose carboxylic esters are obtained under heterogeneous reaction conditions where cellulose is derivatized, e.g., in a bath containing an anhydride and a mineral acid catalyst. The problems that are associated with this reaction scheme have been discussed elsewhere (Toyoshima 1993), along with the advantages of using a homogeneous reaction scheme, HRS. In the latter, cellulose is dissolved in a non-derivatizing solvent, e.g., LiCl/ N,N-dimethylacetamide, DMAc; tetra(n-butyl)ammonium fluoride/DMSO, or an ionic liquid (El Seoud et al. 2007); the dissolved bio-polymer is then derivatized, e.g., with a functional derivative of a carboxylic acid. Use of the HRS permits control of the degree of substitution (DS) of the product; these are usually regularly substituted along the polymer backbone (El Seoud and Heinze 2005; Heinze and Koehler 2010). Relative to the industrial processes, the HRS is more expensive, this calls for optimization of the steps involved, and recycling, e.g., of the electrolyte employed and the solvent (Marson and El Seoud 1999; El Seoud et al. 2000).

In previous studies on cellulose derivatization by the HRS, the emphasis has been on increasing the reaction efficiency, e.g., in terms of obtaining a targeted DS with minimum excess of the acylating agent, expressed as, e.g., acetic anhydride/anhydroglucose unit, Ac₂O/AGU. The reaction conditions, including temperature, time and Ac₂O/AGU were found to be dependent on the structural characteristics of cellulose, including its degree of polymerization, DP; nature, microcrystalline, MCC, or fibrous; more vigorous conditions were employed with the latter type of cellulose.

The present study has been carried out in order to quantify this dependence. Thus, we have determined the relationship between DS and Ac_2O/AGU for MCC and for two fast-growing fibrous celluloses, cotton linters and sisal, both mercerized, M-cotton and M-sisal, respectively. We have found that the abovementioned dependence can be described by an

exponential decay equation, and that the reaction efficiency is qualitatively dependent on DP, and linearly dependent on the aggregation number, N_{agg} , of cellulose aggregates in solution. Our results, therefore, show the relevance of the dissolution step and the physical state of the dissolved cellulose to the efficiency of acetylation and, presumably, acylation in general.

Experimental

Materials

The cellulose samples employed were MCC (Avicel PH 101, FMC, Philadelphia), low average molar weight cotton linters (Indústria Fibra, Americana, São Paulo), and sisal (Lwarcel, Lençois Paulista, São Paulo). Chemicals were purchased from VETEC (São Paulo), Mallinckrodt, and Merck. Before use, LiCl was dried by heating at 200 °C for 3 h, cooled under reduced pressure, and kept in a desiccator. DMAc was distilled from CaH₂, and kept over activated type 4 Å molecular sieves.

Cellulose mercerization

Cellulose from cotton linters and sisal were mercerized in 20% NaOH solution (solid: liquor ratio 1:50 w/w; under nitrogen atmosphere) at 0 °C during 4 and 1 h, respectively. The alkali-swollen material was washed with distilled water until base-free (Buschle-Diller and Zeronian 1992; Ramos et al. 2005). The airdried mercerized products were kept in oven under reduced pressure, at 60 °C, until constant weight.

Cellulose characterization

Cellulose characteristics were determined as indicated elsewhere, for the viscosity-based degree of polymerization ($\overline{DP}v$) (ASTM 2001), index of crystallinity (Ic) (Buschle-Diller and Zeronian 1992), and α -cellulose content (Browning 1967; TAPPI 1988).

Dissolution and acetylation of the celluloses

These two consecutive steps were carried out according the published procedures, according to the reaction scheme below (El Seoud et al. 2000):

Determination of DS and the distribution of the acetate groups in the anhydroglucose unit

The DS of cellulose acetates was determined by ¹H NMR, by using Brucker AC-200 spectrometer (80 °C; 392 scans). Samples were dissolved in DMSO- d_6 (10 mg mL⁻¹), in the presence of a drop of trifluoroacetic acid (Iwata et al. 1992; Edgar et al. 1995). The distribution of the acetyl moiety among the carbon atoms of the AGU was calculated from the ¹³C NMR spectrum by integrating the CH_3CO - peaks of cellulose acetates in DMSO-d₆ (50 mg/mL), in the presence of 20 mg/mL of Cr³⁺-acetyl-acetonate. The ¹³C NMR spectrum was recorded at 80 °C; 8,000 scans were added, with pulse delay of 5 s; the inverse-gated decoupling program was employed for data acquisition (Braun and Berger 2004; Sei et al. 1985). The chemical shifts employed for CH_3CO were: 168.71-168.93 ppm (C₂), 169.11-169.60 ppm (C₃), 169.83–170.04 ppm (C₆) (Kowsaka et al. 1988; 20, Tshunashima and Hattori 2000).

Determination of N_{agg} by static light scattering (SLS) measurements

The dissolution of cellulose samples was carried out as shown in Fig. 1, the final cellulose and LiCl concentrations were 5- and 6 wt%, respectively. More dilute cellulose samples were obtained by diluting the stock solution with 6 wt% LiCl/DMAc. Before performing the static light scattering measurements, each cellulose solution was centrifuged at 16,000g for 2 h, and the upper part of solution was carefully transferred to the SLS cylindrical cell. We have employed Malvern 4700 light scattering system, operating with a variable power Ar-ion laser source (Spectra Physics model 177, 488 nm); optical alignment was checked over the angular range 10-120° by using distilled, dust-free toluene. The scattering data (scattering intensity versus angle at different cellulose concentrations (1.39-3.39; 0.66-2.37; 1.83-3.90 wt% for MCC, M-cotton, and M-sisal, respectively) were analyzed by using the Zimm plot (Hiemenz and Lodge 2007). The exact concentration of cellulose in every solution was determined by precipitation in ethanol, washing with water until the washing was Cl⁻-free, drying at 105 °C for 2 h, cooling, and weighting. Values of (ôn/ ∂c), the refractive index increment were calculated



Fig. 1 Schemes for the dissolution and acetylation of cellu-loses under the HRS

from the dependence of the refractive indices of the same solutions employed in the SLS measurements on the concentration of dissolved biopolymer, by using Rudolph model J357 digital refractometer. These plots were strictly linear (correlation coefficients ≥ 0.996), the corresponding ($\partial n/\partial c$) values were 0.044, 0.123, and 0.069 mL/g for MCC, M-cotton, and M-sisal, respectively; these values are in the range of those determined for different cellulose samples in the same solvent (Dupont and Harrison 2004). The value of N_{agg} was calculated by dividing the weight-average molecular weight by [($\overline{DP}v$) × 162].

Results and discussions

Characterization of the biopolymer and its acetate; effects of mercerization on the structural characteristics of cellulose

The values of $\overline{DP}v$ (±3.0) for MCC, untreated cotton linter and sisal celluloses were found to be 150, 400 and 642, respectively. The $\overline{DP}v$ of M-cotton was the same as that of the starting sample; $\overline{DP}v$ of sisal decreased by ca. 10% after mercerization, vide infra, Table 2. Mercerization increased the α -cellulose content of cotton from 91 to 96%, and that of sisal from 89 to 97%. The latter result may be important for the derivatization of M-sisal, because the presence of hemicelluloses may affect cellulose aggregation, hence accessibility (Ciacco et al. 2010; Henniges et al. 2010). For fibrous celluloses, the abovementioned treatment decreased Ic from 0.80 and 0.67 to 0.72 and 0.64, for M-cotton, and M-sisal, respectively.

Unlike native sisal that can be dissolved in LiCl/ DMAc, dissolution of cotton linters in the same solvent is sluggish; mercerization is often required in order to speed up this step. The reason is that sisal crystallites are smaller than those of cotton linters, i.e., their dissolution does not require pre-treatment in order to decrease their size. The penetration of the solvated LiCl/DMAc complex into the polymer chains is probably more efficient for mercerized celluloses, due to the marked effect of this treatment on the average size, and size distribution of the "pores" at the biopolymer fiber surface (Ramos et al. 2005).

Characterization of cellulose acetates

The acetylation reactions have been carried out in duplicate; the agreement between the DS of these runs indicated good reproducibility, as expected for the HRS. The DS values of cellulose acetates were determined from the ratio between the area of the AGU hydrogens ($\approx 2.90-5.10$ ppm) and the corresponding one for the methyl group of the acetate moiety (\approx 1.70–2.20 ppm; Edgar et al. 1995). Analysis of cellulose acetates by ¹³C NMR allows the determination of the distribution of the acetyl moiety among the three OH groups of the AGU (Kowsaka et al. 1988; Buchanan et al. 1991). Although peak overlapping precluded detailed analysis of the dependence of this distribution on DS, all spectra (not shown) have indicated that the least sterically hindered C6-OH is more reactive than C2-OH and C3-OH, in agreement with previous results (Marson and El Seoud 1999;

Ass et al. 2006).

Correlation between DS and the molar ratio Ac_2O/AGU

The acetylation of different cellulose samples was carried out under fixed reaction conditions, 4 h at 110 °C, except for cellulose concentration, 3.3 and 2.0 wt%, for MCC and fibrous celluloses, respectively. The time employed was dictated by a recent result that showed that the value of DS of M-sisal

Table 1 Results of the acetylation of cellulose samples under fixed reaction conditions, 4 h at 110 $^{\circ}\mathrm{C}$

Cellulose	Ac ₂ O/AGU ^a	$DS \pm 0.05$	Reaction efficiency ^b
мсс	0.5	0.20	40
	1.0	0.66	66
	1.7	1.3	76
	2.0	1.66	83
	2.5	1.85	74
	3.0	2.07	69
	4.0	2.3	c
	6.0	2.7	с
M-cotton	1.0	0.28	28
	1.5	0.6	40
	1.7	0.7	41
	3.0	1.6	53
	6.0	2.4	с
	9.0	2.65	c
	12.0	2.9	c
M-sisal	1.0	0.30	30
	1.5	0.90	60
	1.7	1.0	59
	2.0	1.3	65
	3.0	1.7	57
	6.0	2.4	с
	9.0	2.8	с

^a Molar ratio acetic anhydride/AGU

^b Acetylating efficiency = $(100 \times (DS_{obtained}/DS_{stoichiometric}))$ ^c The reason for not reporting these efficiencies is discussed in the text

may decrease after acetylation for 5 h at 110 °C, due to side reactions (Ciacco et al. 2010). From the dependence of DS on Ac₂O/AGU, shown in Table 1, we have calculated the reaction efficiency by the equation:

Efficiency = $(100 \times (DS_{obtained}/DS_{stoichiometric}))$

In principle, the reaction efficiency could have been calculated by use of an equation that takes into account the DS obtained, the concentration of acetic anhydride, and the time required to reach the maximum DS, t_{max} , e.g., Efficiency = $100 \times \{[(DS_{obtained}/DS_{stoichiometric}) \times (4/t_{max})]/[3/(Ac_2O/AGU)]\}; t_{max}$ is in hour, and the figures (4 and 3) refer to the (fixed) reaction time employed, and the maximum possible DS, respectively. Therefore, the reaction efficiency decreases as a function of increasing Ac_2O/AGU, and



Fig. 2 Comparison of the efficiencies of acetylation of cellulose samples under fixed reaction conditions (4 h, 110 °C)

increases as a function of decreasing t_{max} . Application of this equation, however, is outside the scope of the present work because the evolution of DS as a function of time has not been determined. In Table 1, therefore, we do not report efficiencies for Ac₂O/ AGU > 3. Up to Ac₂O/AGU = 3, however, *all* DS obtained were <3. Consequently, t_{max} has not been reached, i.e., the comparison of acetylation efficiencies of the three cellulose samples (shown in Fig. 2) is meaningful.

The results of Table 1 show that the reactivity follows the order: MCC > M-sisal > M-cotton. In fact, we have found that the dependence of DS on Ac_2O/AGU can be nicely fitted by using the following first order exponential decay equation:

$$DS = DS_o - A e^{-[(Ac_2O/AGU)/B]}$$
(1)

where (A) and (B) are regression coefficients, and DS_o is the calculated maximum degree of substitution, achieved under the conditions of each experiment. These correlations are shown in Fig. 3, and the results of the regression analysis are listed in Table 2, along with $\overline{DP}v$, Ic, and N_{agg}, the latter was measured by SLS. The relevant quantity of the above-

mentioned equation is the regression coefficient (B), whose values quantifies the dependence of DS on Ac_2O/AGU ; small (B) means a more efficient reaction.

The data of Tables 1 and 2 and Fig. 3 raise the following question: What are the factors that control the efficiency order of this reaction, hence the correlation between DS and Ac₂O/AGU? We consider two factors, namely, cellulose structural characteristics (Ic and DP), and its aggregation state in solution. The first two columns of Table 2 show that the order of Ic (MCC > M-cotton > M-sisal) does not follow the above-mentioned order of reactivity (or the order of B). It is expected that once dissolved, Ic of the starting cellulose has no bearing on DS because the difference in cellulose accessibilities that arise from differences in Ic no longer exist. This conclusion agrees with previous studies that indicated no obvious correlation between cellulose solubility and its crystallinity (Lennholm et al. 1994; Sjöholm et al. 1997). Additionally, we have repeatedly shown that the rate constants and activation parameters for the decrystallization of MCC and fibrous celluloses are very similar, albeit the differences in Ic and $\overline{DP}v$ of the starting material (Marson and El Seoud 1999; Ramos et al. 2005). That is, cellulose decrystallization that precedes its dissolution is not a rate limiting step in its acetylation, hence is not expected to control the DS obtained.

There is a qualitative dependence of DS on DP because the value of the coefficient (B) is smallest for MCC, the most reactive cellulose. The following factors may have contributed to the (apparent) lack of a quantitative correlation of DS with DP: The number of cellulose sample examined is small, examination of a larger number is required; both fibrous cellulose have relatively low DP and the ratio $(\overline{DP}v)_{M-sisal}/(\overline{DP}v)_{M-cotton}$ is not particularly large (1.45); M-cotton and M-sisal may have different hemi-

Fig. 3 Dependence of DS on the ratio (Ac₂O/AGU) for different cellulose samples, after acetylation for 4 h at 110 °C. The points are experimental, the curves represent first order exponential decay fitting



Table 2 Characteristics of celluloses and their solutions in LiCl/DMAc, along with the results of the regression analysis according to the equation: $DS = DS_0 + Ae - [(Ac_2O/AGU)/B]$

Cellulose	$\overline{DP}v$	Ic	N_{agg}	DSo	А	В	r ²
MCC	150	0.83	11	2.87	3.4475	2.0818	0.9944
M-cotton	400	0.72	40.1	2.92	3.7368	3.0621	0.9965
M-sisal	581	0.64	21.0	2.81	3.6791	2.3980	0.9915

cellulose contents, these affect the solution state of the dissolved cellulose samples, hence their accessibilities.

Under typical conditions of synthesis, the dissolved polymer is not molecularly dispersed but present in a colloidal state, designated as "fringed micelles" (El Seoud and Heinze 2005). In fact, aggregate-free solutions of polysaccharides are hard to obtain, and are stable in diluted states only, ca. 1 wt% cellulose (Rinaudo 1993). Experimental SLS and SEC data have indicated the presence of colloidal aggregates in the LiCl/DMAc solvent system (Morgenstern and Kammer 1999; Hasegawa et al. 1993; Aono et al. 2004, 2006; Ciacco et al. 2008; Dawsey and McCormick 1990; Hattori et al. 2002; Matsumoto et al. 2002; Striegel and Timpa 1995); molecularly dispersed cellulose solutions are obtained at low polymer- and high LiCl concentrations (Roder et al. 2000). Non-cellulosic materials affect the state of the biopolymer aggregation; whereas hardwood Kraft pulps were found to be completely soluble in this solvent system, softwood Kraft pulps were not, due to relatively higher contents of mannan, lignin, and nitrogen containing compounds (Sjöholm et al. 1997). Therefore, one of the reasons that mercerization is expected to lead to better results, i.e., higher DS, is the effect of (basemediated) removal of non-cellulosic material on the physical state of cellulose in solution.

The preceding discussion points out to the possibility that the aggregation of the cellulose chains, and the accompanied decrease in the biopolymer accessibility is important to the efficiency of acetylation. In fact, the correlation between (B) and N_{agg} is perfectly linear with a positive slope:

$$(B) = 1.709 + 0.034 N_{agg}; \quad r = 0.9989$$
 (2)

where (r) is the regression coefficient. That is, the reaction efficiency is inversely dependent on the

aggregation number of the cellulose fringed micelle. To our knowledge, this is the first report that quantifies the effect of this phenomenon on the accessibility, hence reactivity of cellulose. This linear correlation is interesting because the biopolymer concentrations of MCC and mercerized fibrous celluloses were different, 3.3 and 2 wt%, respectively; increasing cellulose concentration results in an increase in the molar mass of the fringed micelle, although its dimensions increase only slightly. This concentration effect, however, is probably much less pronounced for MCC because the length of the short cellulosic chain is practically equal to its persistent length, i.e., there is practically no chain coiling (El Seoud and Heinze 2005). The linear correlation between (B) and N_{agg} indicates, therefore, that the higher cellulose concentration has not enhanced the aggregation of MCC. More work should be done, however, in order to test the generality of these conclusions. In particular, a larger number of cellulose samples that cover a wider range of DP should be examined in order to increases the statistical validity of the correlations, and to assess unambiguously the relative importance of DP and the aggregation state of cellulose to its reactivity as quantified, e.g., by Eq. 1; we hope to contribute further to this undertaking.

Conclusions

The efficiency of the aceylation reaction, as measured by the dependence of DS on the molar ratio Ac_2O/AGU has been quantified for three cellulose samples. The limited body of data available indicates that this efficiency is a function of the DS of the dissolved cellulose, and its accessibility in the aggregates formed. In general, the latter depends on the concentrations of cellulose (in particular for fibrous celluloses) and LiCl, as well as the experimental conditions, temperature, agitation time and speed. Therefore, meaningful comparison of the efficiency of these reactions rests on the use of comparable experimental protocols.

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