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A convenient solvent system for cellulose dissolution and derivatization: Mechanistic aspects of the acylation of the biopolymer in tetraallylammonium fluoride/dimethyl sulfoxide

Romeu Casarano, Haq Nawaz, Shirley Possidonio, Valdinéia C. da Silva, Omar A. El Seoud*

Institute of Chemistry, University of São Paulo, P.O.B. 26077, 05513-970 São Paulo, S.P., Brazil

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ABSTRACT

This work is concerned with the dissolution of cellulose in tetraallylammonium fluoride/DMSO; the thermal stability of electrolyte solution, and relevant mechanistic aspects of the biopolymer acylation. EMF measurements (fluoride ion-selective electrode) showed that the electrolyte is present as monohydrate. ^{1}H NMR spectroscopy showed that it does not undergo elimination via ylide intermediate, even after heating for 21 h at 70 °C. A solution of TAAF in DMSO readily dissolves microcrystalline and fibrous celluloses (cotton and eucalyptus); the dissolved biopolymer can be derivatized into esters by reaction with carboxylic acid anhydrides. Cellulose ethanoate, butanoate, hexanoate, and mixed esters, ethanoate/butanoate, ethanoate/hexanoate were conveniently synthesized under homogeneous reaction conditions (3 h at 60, 80, and 100 °C). Using longer reaction times (12, 18 h) lead to esters of low degree of substitution, due to fluoride-ion mediated ester-hydrolysis. The intermediate formation of acyl fluorides in this medium has been confirmed by FTIR spectroscopy.

1. Introduction

There is a growing interest in using biodegradable polymers from renewable raw materials instead of the (finite, almost non-biodegradable) petroleum-based counterparts, e.g., polyethylene and polypropylene. Cellulose is the most abundant natural raw material, it constitutes about one third of all plant material, and it is the main constituent of the plant cell walls (Imeson, 1999). The strong inter- and intra-molecular hydrogen bonding within the biopolymer mean that it cannot be processed by extrusion; presumably it decomposes before melting. The solutions of this problem include regeneration of cellulose from its solution in, e.g., *N*-methylmorpholine-*N*-oxide (the so-called Lyocell process) (Chavan & Patra, 2004; Fink, Weigel, Purz, & Ganster, 2001), or transformation into a soluble derivative that can be processed by extrusion into a bath, e.g., cellulose diethanoate/acetone (Rustemeyer, 2004). Cellulose derivatization under (industrial) heterogeneous reaction conditions is associated with a series of problems that have been discussed elsewhere (Toyoshima, 1993). In the homogeneous reaction scheme, the biopolymer is dissolved in a medium (physical dissolution; no covalent bond formation), then derivatized. The most important examples of these solvent systems are LiCl/*N*,*N*-dimethylacetamide, DMAc, and tetra(1-butyl)ammonium fluoride trihydrate/DMSO (TBAF/DMSO; hereafter, TBAF refers to the trihydrate). More recently, ionic liquids, especially imidazole-based ones have gained popularity, albeit their high cost, because of their structural versatility; they are composed only of ions; no additional electrolyte is required (Dawsey & McCormick, 1990; El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007; El Seoud, Marson, Ciacco, & Frollini, 2000; Fidale, Possidonio, & El Seoud, 2009; Fink et al., 2001; Heinze, Lincke, Fenn, & Koschella, 2008; Le Moigne, Spinu, Heinze, & Navard, 2010; Marson & El Seoud, 1999a, 1999b; Rohleder & Heinze, 2010; Striegel, 1997).

We focus here on quaternary ammonium fluorides, first reported by Heinze, Dicke, Koschella, Kull, and Koch (2000). Solution of TBAF in DMSO is capable of dissolving celluloses, including those of very high degree of polymerization (DP) (Ass, Frollini, & Heinze, 2004; Ciacco, Liebert, Frollini, & Heinze, 2003). This solvent system has been successfully employed for the derivatization of celluloses by employing variable reaction times, temperatures, and derivatizing agent/cellulose molar ratios (Ass et al., 2004; Heinze et al., 2000). Depending on the experimental conditions TBAF, like the corresponding hydroxide (the F^- and OH^- ions are isoelectronic; Kluge & Weston, 2005), may be susceptible to Hofmann elimination (see Scheme 1) (Albanese, Landini, & Penso, 1998; Sharma & Fry, 1983).

* Corresponding author. Tel.: +55 11 3091 3874; fax: +55 11 3091 3874.
E-mail address: elseoud@iq.usp.br (O.A. El Seoud).

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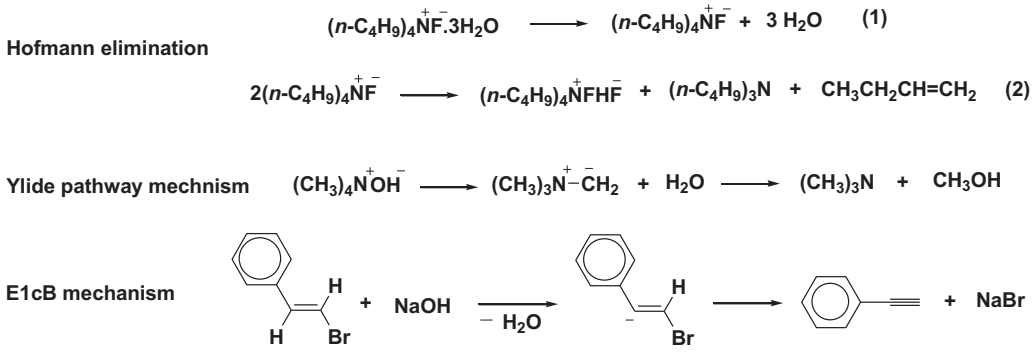


Scheme 1. Illustration of Hofmann elimination of TBAF, degradation mechanism of tetramethylammonium cation by an ylide pathway, and E1cB elimination of trans-β-bromostyrene (Chempath et al., 2010; Makosza & Chesnokov, 2003; Sharma & Fry, 1983).

Although tetramethylammonium fluoride and benzyltrimethylammonium fluoride do not undergo Hofmann degradation (because of the absence of β hydrogen in the N^+-R chains), their solutions in DMSO are not useful media for cellulose dissolution/derivatization. The former electrolyte does not dissolve cellulose; the latter has a very limited biopolymer dissolution capacity, this was attributed to its low solubility in the solvent (Koehler & Heinze, 2007). Note that tetramethylammonium fluoride and benzyltrimethylammonium fluoride are, in principle, subject to another degradation mechanism, via ylide intermediate pathway, as illustrated in Scheme 1 for the former (Chempath, Boncella, Pratt, Henson, & Pivovar, 2010). The ylide mechanism is akin to the E1cB counterpart, except that the species produced by proton elimination is a zwitterion, see Scheme 1.

We thought that an electrolyte that is appreciably soluble in DMSO, and is free from elimination reactions would constitute a welcomed addition to this important solvent system. The electrolyte chosen, tetraallylammonium fluoride (TAAF) was synthesized by the reaction of triallylamine and allyl chloride, followed by ($Cl^- \rightarrow OH^-$) ion-exchange and neutralization of the resulting hydroxide by HF solution. It was found to be soluble in DMSO, the resulting solution easily dissolves microcrystalline- and fibrous celluloses (cotton and eucalyptus). Carboxylic esters, ethanoate, butanoate, and hexanoate, and mixed esters, ethanoate/butanoate and ethanoate/hexanoate were successfully synthesized under homogeneous reaction conditions.

In addition to the use of TAAF/DMSO as cellulose solvent, we have investigated mechanistic aspects of this system. TAAF is not subjected to the Hofmann elimination reaction; degradation by the ylide pathway (see Scheme 1) is a possibility. We have employed ^{1}H NMR spectroscopy in order to show that the latter mechanism is not operative. The fluoride ion can act as a nucleophilic catalyst for acyl-transfer reactions, e.g., the hydrolysis of ethanoic and succnic anhydrides (Bunton & Fendler, 1967) and of some esters (Ueki, Kai, Amemiya, Horino, & Oyamada, 1988), via the intermediate formation of acyl fluoride. The same species is formed from acetyl chloride and tetraethylammonium fluoride in the presence of ethanoic acid (Emsley, Gold, Hibbert, & Szeto, 1988). We have employed FTIR in order to show the formation of RCOF when TAAF is mixed with $(RCO)_2O$ in DMSO. The dependence of the degree of ester substitution, DS, on the biopolymer acylation time is explained on the bases of fluoride ion-mediated cellulose ester hydrolysis.

2. Experimental

2.1. Materials

The reagents were purchased from Acros, Aldrich, or Merck and were purified as indicated elsewhere (Armagero & Chai, 2003). Aqueous solution of HF (40 wt%); methanol; DMSO-d_6; trifluoroethanoic acid (99%), and $NaClO_4$ were used as received. Microcrystalline cellulose, MCC; Avicel PH 101 was from FMC (Philadelphia; DP_v = 175; v = viscosity). Sheets of cotton (DP_v = 920) and eucalyptus (DP_v = 1049) celluloses were supplied by Lwarcel Cellulose and Paper (Lençóis Paulista, São Paulo) and Nitro Química S.A. (São Paulo), respectively. The sheets were cut into stripes and grounded in a water-cooled cutting mill (Thomas Scientific model 3383-L10, Swedesboro) against a 10-mesh stainless steel sieve. All fibrous cellulose samples were further sieved through a 100–200 mesh sieve (Fritsch Analysette 3 Spartan, Idar-Oberstein). The cellulose samples were dried in a vacuum-oven at 60 °C for 24 h, and were kept in tightly stoppered flasks.

2.2. Equipment

The melting points were determined with Electrothermal IA 6304 mp apparatus (London). Elemental analyses were carried out at the central analytical facility of this Institute, using Perkin-Elmar Elemental Analyser CHN 2400. The value of DP_v was determined using shear-dilution Cannon-Fenske viscosimeter (Schott), inserted in Schott AVS 360 automatic viscosity determination equipment. ^{1}H and ^{13}C NMR measurements were recorded with Varian Innova-300 or Bruker DPX 300 NMR spectrometers (both operating at 300 MHz for ^{1}H). EMF measurements were carried out with Fisher Accumet-50 ion-meter, equipped with a thermostated glass measuring cell, closed with a PTFE cover, through which the electrodes are inserted (*vide infra*). IR spectra were recorded with Bruker Vector-22 FTIR spectrophotometer.

2.3. Material characterization

DP_v was determined (25 °C) from the intrinsic viscosity of cellulose solution in CUEN/water (1:1, v/v) according to the recommended method (ASTM D1795-94, 2001). Plots of ln(relative viscosicity/[Cell-CUEN]) versus [Cell-CUEN] were strictly linear, whose intercepts are the intrinsic solution viscosities. The value of DS of cellulose simple carboxylic esters was determined by the solvatochromic indicator method (Casarano, Fidale, Lucheti, Heinze, & El Seoud, 2011); the DS of few samples was also determined by titration (ASTM D871-96, 2004); the results of both methods were in good agreement. The total- and partial DS of cellulose acetate/other alkanoate esters were determined by ^{1}H NMR, as given elsewhere, by comparing the peak areas of the AGU (seven) hydrogens with those of the acyl moieties. For example, CH_3CO plus $CH_3(CH_2)_2CO$ (these two peak overlap) and $CH_3(CH_2)_2CO$ for cellulose acetate/butyrate (Heinze, Liebert, & Koschella, 2006; IWata, Azuma, Okamura, Muramoto, & Chun, 1992; Possidonio, Fidale, &

El Seoud, 2010; Tezuka, 1993). The uncertainty in DS was found to be 0.1 unit.

2.4. Synthesis of tetraallylammonium fluoride; Scheme 2

The synthesis of tetraallylammonium chloride (TAACl) was carried out in a stainless steel reactor provided with an inner glass cup, covered with PTFE cover. Triallylamine, 24 mL, 0.14 mol; allyl chloride, 17 mL, 0.21 mol; and 56 mL of acetonitrile were mixed in the cup; the reactor was purged with oxygen-free nitrogen and closed; the pressure was increased to 30 atm, the temperature was raised to 120 °C, and the mixture was allowed to react under stirring for 24–26 h. After removing all volatiles, the product was washed several times with toluene, the solid filtered off, and then dried under reduced pressure at 35 °C for 24 h. Yellowish solid; yield = 79%; mp = 156.5–157.0 °C. Anal. Calcd. for $C_{12}H_{20}NCl$: C, 67.4%; H, 9.5%; N, 6.5%. Found: C, 66.2%; H, 9.8%; N, 6.6%. ^{1}H NMR (DMSO-d_6; (m) and (d) stand for multiplet and doublet, respectively): 5.68 ppm, $H3_a$, d, J_{H3a-H2} = 15.0 Hz; 5.61 ppm, $H3_b$, d, J_{H3b-H2} = 9.0 Hz; 6.19–6.05 ppm, H2, m; 3.94 ppm, H1, d, J_{H1-H2} = 6.0 Hz.

The chloride was converted into the corresponding hydroxide by ion exchange on a macro-porous resin (Purolite SGA55OOH, 1.10 equiv. OH^-/L). One liter of a 0.1 M methanolic solution of TAACl was passed through a glass column containing 150 mL of the resin. The completeness of the (Cl^-/OH^-) halide exchange was checked by treating a sample of the effluent with acidified $AgNO_3$ solution. The pH of the hydroxide solution was brought to *ca.* 7 (expanded scale pH-paper) by adding methanolic HF solution. Finally, the solvent was evaporated under reduced pressure (2 mmHg) at room temperature to yield a viscous, highly hygroscopic, yellowish liquid (see Fig. SM-1(a) (Fig. 1(a) of Supplementary Material)). Solvent evaporation was also carried out at 40–60 °C, in the presence of 3 mole% (relative to TAAF concentration) of propyl gallate, PG, to yield a brownish-red liquid, see Fig. SM-1(b).

For elemental analysis, TAAF was converted into the corresponding (non-hygroscopic) perchlorate salt, by the addition of excess (50%) of $NaClO_4$ solution, followed by filtration, washing the yellowish solid obtained with water, and drying under reduced pressure at room temperature. Anal. Calcd. for $C_{12}H_{20}NClO_4$: C, 51.9%; H, 7.2%; N, 5.0%. Found: C, 51.8%; H, 7.1%; N, 4.9%. ^{1}H NMR of TAAF (DMSO-d_6): 5.68 ppm, $H3_a$, d, J_{H3a-H2} = 18.0 Hz; 5.61 ppm, $H3_b$, d, J_{H3b-H2} = 9.0 Hz; 6.17–6.03 ppm, H2, m; 3.94 ppm, H1, d, J_{H1-H2} = 7.0 Hz. ^{13}C NMR (75 MHz, DMSO-d_6): 125.6 ppm (C3); 127.5 ppm (C2); 60.6 ppm (C1).

2.5. Determination of the water content of TAAF

Fisher Accumet-50 ion-meter was employed, along with Corning double-junction Ag/AgCl reference electrode and Orion 940900 ion-selective electrode (ISE, fluoride); all measurements were carried out at 25 ± 0.1 °C. The procedure employed was that published elsewhere (Fidale, Koehler, Prechtl, Heinze, & El Seoud, 2006). Briefly, the halide ion concentration (hence TAAF concentration) was calculated from the EMF potential measured and the equation:

$$\text{Potential measured, mV} = -332.8(\pm 0.7) - 25.4(\pm 0.1)\ln[F^-]$$

$$r = 0.9999$$

obtained from Nernst law plot, constructed by employing NaF solutions. The water content of TAAF/DMSO was calculated from the difference between weights of the starting electrolyte, and that calculated from Nernst law equation. A duplicate determination has indicated that the electrolyte is present as monohydrate. Hereafter, TAAF refers to $(C_3H_5)_4NF{\cdot}H_2O$.

2.6. Evaluation of the thermal stability of TAAF in DMSO

The thermal stability of TAAF was assessed by ^{1}H NMR spectroscopy; toluene was used as an internal reference. The following solutions were prepared by weight in 5 mL round-bottom flasks: TAAF in DMSO-d_6 (solution A; 0.16 mol/L) and toluene in DMSO-d_6 (solution B; 0.42 mol/L). The one containing the TAAF was fitted with a reflux condenser and heated at 70 ± 2 °C under a slow stream of dry, oxygen-free nitrogen. Samples were withdrawn after 2, 4, 6, 9, and 21 h; after cooling they were weighted, mixed with a known weight of the solution (B), and the mixtures were analyzed. The dependence of TAAF on time was calculated by comparing the peak areas of both substances, at 7.05–7.55 ppm, aromatic hydrogens of toluene; 6.25–5.95 ppm, 5.72–5.55 ppm, and 3.95–3.83 ppm, discrete hydrogens of TAAF.

2.7. Effect of heating time of cellulose triethanoate/TAAF–DMSO on the degree of substitution of the ester

The effect of heating on the DS of cellulose triethanoate in TAAF/DMSO was evaluated. A solution of TAAF (6.6 g) in DMSO (80 mL) was prepared and divided into two equal parts. Commercial cellulose triethanoate (CA 398-6; DS = 2.7; Eastman; 0.55 g) was then dissolved in each solution, to give samples (A) and (B). Both were heated under nitrogen, at 60 ± 2 °C, for 6 and 18 h, respectively. They were added to ethanol, the precipitated cellulose ethanoate was filtered, washed with ethanol twice, dried, and its DS determined as given above.

2.8. Detection of the formation of acyl fluoride by FTIR spectroscopy

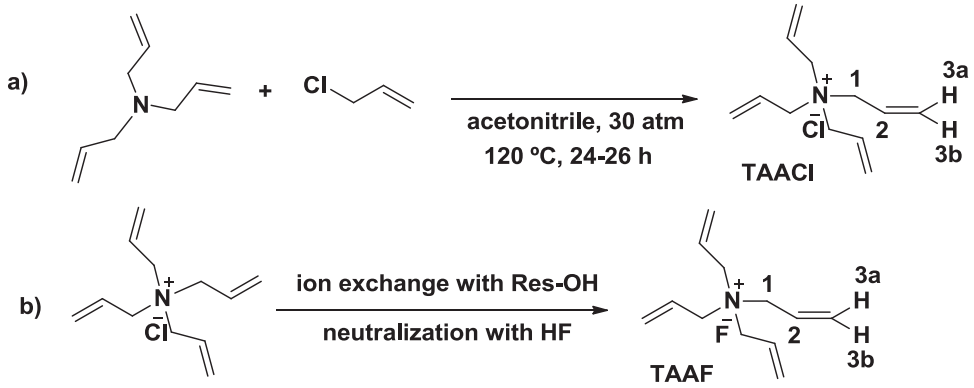
In round-bottom flasks provided with stoppers, the following solutions were prepared in DMSO where the molar concentration of each species was 0.43 mol/L: TAAF, 0.674 g/8 mL; ethanoic anhydride, 0.194 g/4.4 mL; hexanoic anhydride, 0.367 g/4.0 mL. The FTIR spectrum was recorded for each solution. Equal volumes of the stock solution of TAAF plus *each anhydride* solution were mixed, quickly transferred to the IR cell, and the spectra of the mixtures were recorded immediately, and at time intervals during 8 h. The following are the experimental conditions: spectrum background, air; CaF_2 cell, pathlength 0.025 mm; 32 scans were added at 0.5 cm^{-1} digital resolution.

2.9. Dissolution and acylation of MCC and fibrous celluloses in TAAF/DMSO

The MCC sample, 0.5 g, was introduced into a three-neck round-bottom flask containing a solution of TAAF (3.3 g) in DMSO (30–40 mL). After 15 min of mechanical stirring at room temperature, under N_2 atmosphere a clear solution was obtained. The procedure to dissolve fibrous celluloses was the same, except that clear solutions were obtained after 30 min at room temperature plus 1 h at 60 °C.

After dissolution of the biopolymer, the required amount of carboxylic acid anhydride was added and the reaction was allowed to proceed, under mechanical stirring and N_2 atmosphere, at 60, 80 or 100 °C for the required length of time. The same procedure was employed for the synthesis of cellulose mixed esters (ethanoate/butanoate and ethanoate/hexanoate), in which both anhydrides were introduced simultaneously, in equal molar concentrations.

The acetates were recovered from the reaction mixtures by precipitation in ethanol (3 × 300 mL) followed by centrifugation at 3500 × *g* (60 min; IEC Centra MP4R). In case of the other esters, and the mixed ones the treatment with ethanol was carried out at



Scheme 2. Reaction scheme showing the three steps of the synthesis of TAAF, namely, the reaction of triallylamine with allyl chloride; ($Cl^- \rightarrow OH^-$) ion-exchange; the neutralization of the quaternary ammonium hydroxide with HF. The numbering of H/C atoms is that used to describe the NMR results.

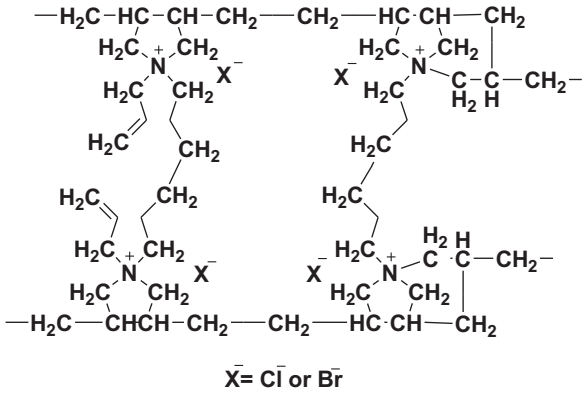
ca. 60 °C, in order to remove the adsorbed acid, *especially hexanoic acid*. Before DS determination, all cellulose esters were dried under reduced pressure, in the presence of P_4O_{10}, at 50–60 °C, for 48 h.

3. Results and discussion

3.1. Synthesis of TAAF

As shown in Scheme 2, TAAF was synthesized via the corresponding chloride, followed by ($Cl^- \rightarrow OH^-$) anion exchange, neutralization by HF, and solvent removal at room temperature, under reduced pressure. Attempts to evaporate methanol at higher temperatures gave a product that was not completely soluble in DMSO (suspended particles). This result may indicate polymerization of a part of TAAF, because TAACl and TAABr undergo free radical polymerization, to form linear as well as crosslinked cyclopolymers (Marek, Fukuta, & Kunitake, 1993; Matsumoto, Kohama, & Oiwa, 1990; Matsumoto, Mano, Oiwa, & Butler, 1989), see Scheme 3. The following result suggests that polymerization occurs only when the TAAF solution in methanol becomes very concentrated. A DMSO-soluble TAAF sample was obtained when *ca.* 80% of methanol was evaporated at 40–60 °C, followed by removing the remaining solvent at room temperature, under reduced pressure.

In order to test our assumption, we added an efficient free-radical inhibitor, PG (Rosenau et al., 2002) to the methanolic solution of TAAF, before solvent evaporation at higher temperature. This use has resulted in time saving; the resulting electrolyte was completely soluble in DMSO; its ^{1}H NMR spectrum showed the



Scheme 3. Molecular structure of the product (crosslinked cyclopolymers containing monocyclic and bicyclic structural units) that is formed by free radical polymerization of TAACl or TAABr in the presence of *t*-butyl hydroperoxide initiator (Matsumoto et al., 1990; Trifan & Hoglen, 1961).

expected peaks of TAAF. The only difference between TAAF samples prepared by both procedures is one of color, see Fig. SM-1, as result of the oxidation of PG to a deeply colored, highly conjugated chromophore (Rosenau et al., 2002). It is noteworthy to note that the ionic liquids 1-allyl-3-methylimidazolium chloride and 1-allyl-3-(1-butyl)imidazolium chloride do not polymerize when heated at 80–90 °C for several hours (Fidale et al., 2009).

3.2. Composition of the TAAF synthesized and its thermal stability in DMSO

Many quaternary ammonium halides are hygroscopic (Fidale et al., 2006). TAAF is also hygroscopic and is expected to be present as a hydrate. The exact composition of the electrolyte should be known because of the complex role played by water in these media, including: consumption of a part of the acylating reagent; enhancement of the aggregation of the dissolved cellulose chains which decreases their accessibility (Potthast et al., 2002; Sjoholm, Gustafsson, Pettersson, & Colmsjo, 1997; Terbojevich, Cosani, Camilot, & Focher, 1995); phase separation (gelation) of the cellulose/electrolyte-DMSO solution. The latter phenomenon occurs when the electrostatic stabilization of the individual cellulose chains decreases as fluoride ions desorb from the polymer and coordinate with water in the bulk solvent (Oestlund, Lundberg, Nordstierna, Holmberg, & Nyden, 2009). As shown in Section 2, the results of the EMF measurement using ISE have shown that TAAF is present as monohydrate.

The stability of TAAF in DMSO-d_6 was evaluated by registering the ^{1}H NMR spectra of the solution after heating at 70 °C (a typical cellulose acylation temperature) for 2, 4, 6, 9, and 21 h, and comparing the peak areas of TAAF with those of toluene (an internal reference), as given in Section 2. The area ratios of the different groups of TAAF to that of $C_6H_5CH_3$ were found to change negligibility ($97 \pm 3\%$) as a function of heating time. This result indicates that TAAF is thermally stable in DMSO, i.e., it does not undergo the ylide pathway in this solvent. That is, it can be advantageously employed for cellulose derivatization at high temperatures in DMSO.

3.3. Cellulose dissolution in tetraalkylammonium halides/dipolar aprotic solvents

We have found that MCC and fibrous celluloses (cotton and eucalyptus) are insoluble in TAACl/DMAc, TAACl/DMSO, or TAAF/DMAc, but are readily soluble in TAAF/DMSO. For the same solvent, DMSO, the effect of the counter-ion (Cl^- versus F^-) can be readily explained, based on the much stronger hydrogen bonding between the fluoride ion and the OH groups of the AGU (Ass et al., 2004). Electrostatic repulsion between the biopolymer chains, due

Table 1
Results of acetylation of MCC in TAAF/DMSO.[a]

Entry	Ac_2O/AGU[b]	Reaction time (h)	Reaction temperature (°C)	DS of product
1	3	18	60	0.4
2	4.5	18	60	0.9
3	6	18	60	1.2
4	4.5	12	80	1.0
5	6	18	80	0.8

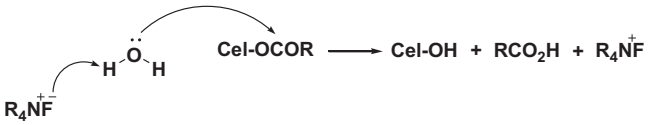
[a] No free radical scavenger was added during TAAF synthesis, *vide* Section 2.
[b] Molar ratio between ethanoic anhydride (Ac_2O) and AGU.

to the adsorbed F^- appears to play an additional role in its dissolution mechanism, as they keep the chains apart (Oestlund et al., 2009). The importance of the higher negative charge-density of F^- to its efficiency of dissolution is in agreement with the conclusion (based on the use of solvatochromic indicators) that the "basicity" (or hydrogen bond acceptance capacity, e.g., AGU-OH···halide ion) of the solution is the dominant factor in dissolving cellulose (Spange, Fischer, Prause, & Heinze, 2003). The results of TAAF in DMAc and DMSO reflect the exceptional cellulose swelling capacity of the latter solvent. This is corroborated by the results of a quantitative study of the swelling of MCC and fibrous celluloses by 36 protic and aprotic solvents, DMSO ranked second only to water (El Seoud, Fidale, Ruiz, D'Almeida, & Frollini, 2008; Fidale, Ruiz, Heinze, & El Seoud, 2008)! Our results for TAAF are similar to those reported elsewhere, e.g., cellulose is insoluble in TBACl/DMSO (Heinze et al., 2000), but is readily soluble in TBAF/DMSO (Ass et al., 2004; Ciacco et al., 2003; Nagel & Heinze, 2010).

As indicated in Section 2, methanol evaporation from the TAAF solution can be accelerated by using PG as a free radical scavenger. The resulting TAAF/DMSO solvent system, although dark in color, has been successfully employed for the acylation of cellulose, *vide infra*.

3.4. Cellulose acylation in the TAAF/DMSO solvent system

After dissolution of MCC in TAAF/DMSO, ethanoic anhydride was added and the reaction was allowed to proceed at 60 or 80 °C for 12 or 18 h. Table 1 shows the reaction conditions and the values of the obtained product DS. Comparison of the first three columns of this table shows that the reaction is not efficient (in terms of DS). A stoichiometric reaction should have produced DS of *ca.* 3, for Ac_2O/AGU molar ratio of 3; this is not the case even when 100% excess anhydride was employed, entries 3 and 5. A possible explanation for this disappointing result is fluoride ion-mediated ester hydrolysis, akin to that observed for benzoate esters in TBAF/DMF (Ueki et al., 1988). In order to test this mechanistic hypothesis, we have carried out the following experiment: a commercial sample of cellulose triethanoate (DS = 2.7) was dissolved in TAAF/DMSO, the solution



Scheme 4. Fluoride ion mediated cellulose ester hydrolysis through a general base-catalyzed attack of water on the acyl group of ester.

was stirred at 60 °C, and the DS of the ester was determined after 6 and 18 h. The results showed a marked decrease in DS, 1.7 and 1.1, respectively, corroborating that fluoride ion-mediated hydrolysis, Scheme 4, is an operative side reaction. Therefore, we decided to use a much shorter reaction time, 3 h, and higher carboxylic acid anhydride/AGU in order to minimize the effect of this side reaction, and to get acceptable DS.

Table 2 shows the reaction conditions and the DS obtained when this approach was employed. The cellulose acetylation was performed in TAAF/DMSO at 60, 80, or 100 °C for 3 h. As it can be seen, the data obtained for MCC in TAAF/DMSO (entries 6–10) are similar to those for low molecular weight cotton linters in TBAF/DMSO (Ass et al., 2004). Entries 11–13 (MCC), as well as entry 16 (cotton), show that the presence of PG (and its oxidation products) has no effect on the DS obtained. Therefore, this use is advantageous because of the saving of time and labor during the synthesis of TAAF.

Entries 14–16 show the expected trend, i.e., fibrous cellulose samples require different conditions from those employed for MCC; the Ac_2O/AGU ratio is *ca.* doubled in order to obtain comparable DS. This difference is well documented in the literature and can be traced to several factors, including, the difference in DP, and in porosity of the cellulose; MCC has mesopores whereas fibrous cellulose have only micropores (El Seoud et al., 2000; Ramos, Assaf, El Seoud, & Frollini, 2005). Additionally, cellulose in these solvents is most probably present as aggregate (called fringed micelles) (El Seoud & Heinze, 2005), whose formation decreases the accessibility of the dissolved chains, hence decreases the acylation reaction rate. As shown in a recent work on the acylation efficiency of celluloses in LiCl/DMAc, the effect of this aggregation is much less pronounced for MCC because the length of the short cellulosic chain

Table 2
Results of acetylation of MCC, or fibrous cellulose, in TAAF/DMSO.

Entry	Cellulose	Ac_2O/AGU[a]	Reaction time (h)	Reaction temperature (°C)	DS of product
6	MCC	6	3	60	1.6 (1.6)[b]
7	MCC	9	3	60	1.9 (2.1)[b]
8	MCC	13	3	60	2.4 (2.3)[b]
9	MCC	6	3	80	1.9
10	MCC	6	3	100	2.2 (2.3)[b]
11[c]	MCC	6	3	60	1.7
12[c]	MCC	6	3	80	1.9
13[c]	MCC	6	3	100	2.1
14	Eucalyptus	13	3	60	1.7
15	Cotton	13	3	60	1.6
16[c]	Cotton	13	3	60	1.8

[a] Molar ratio between Ac_2O and AGU.
[b] Literature values for the acylation of low molecular weight cotton linters (DP_v = 440) in TBAF/DMSO (Ass et al., 2004).
[c] PG, 3 mole% with respect to TAAF was employed during the synthesis of the electrolyte, *vide* Section 2.

Table 3
Synthesis of esters and mixed esters of MCC.[a]

Entry	Cellulose derivative	Reaction time (h)	Reaction temperature (°C)	DS of product
17[b]	Butanoate	3	60	1.4
18[c]	Hexanoate	3	60	1.6
19[d]	Ethanoate/butanoate	3	60	1.5[f]
20[e]	Ethanoate/hexanoate	3	60	1.7[f]

[a] PG was employed during the evaporation of the methanolic solution of TAAF.
[b] Molar ratio between butanoic anhydride:AGU = 6:1.
[c] Molar ratio between hexanoic anhydride:AGU = 6:1.
[d] Molar ratio between ethanoic anhydride:butanoic anhydride:AGU = 3:3:1; both anhydrides were added simultaneously.
[e] Molar ratio between ethanoic anhydride:hexanoic anhydride:AGU = 3:3:1; both anhydrides were added simultaneously.
[f] Refers to total DS. The DS for each acyl moiety is: DS ethanoate: 0.9, DS butanoate: 0.6; DS ethanoate: 0.9, DS hexanoate: 0.8.

is practically equal to its persistent length, i.e., there is practically no chain coiling. Thus the efficiency of acetylation follows the order MCC > mercerized sisal > mercerized cotton, and is inversely dependent on the degree of aggregation of the formed micelles (Ramos, Morgado, El Seoud, da Silva, & Frollini, 2011).

Table 3 shows that TAAF/DMSO can be successfully employed as a reaction medium for the synthesis of cellulose esters of other acids (butanoate and hexanoate) as well as mixed esters, ethanoate/butanoate and ethanoate/hexanoate. The dependence of DS on the anhydride employed is similar to that observed previously, i.e., ethanoic ≈ hexanoic > butanoic; for the mixed esters there is preponderance of the acetate moiety (Possidonio et al., 2010). Based on the use of hydrolysis of these anhydrides in aqueous acetonitrile as a model reaction for cellulose acylation, it was suggested that the dependence of DS on the chain length of the anhydride may be attributed to the balance between two opposing effects: steric crowding and (cooperative) hydrophobic interactions between the anhydride and the cellulosic surface, whose lipophilicity has increased, due to its partial acylation. For the mixed esters, the volume (or rate of diffusion) of the acylating agent is determinant for the partial DS, so that the smaller acyl moiety (ethanoate) is produced in slight excess (Possidonio et al., 2010).

3.5. Mechanistic insight into the role of TAAF: detection of the formation of acyl fluoride by FTIR

The final question to be addressed is about the role of TAAF: does it serve *only* to dissolve the biopolymer, i.e., is it a "spectator"? The reason for the question is that fluoride ion is known to be a powerful nucleophile, especially when it is desolvated (Vlasov, 1993). The formation of acyl fluorides has been experimentally demonstrated in, e.g., the preparation of perhaloalkyl acrylate and methacrylate esters (Pittman, Sharp, & Lundin, 1966); the hydrolysis of acetic anhydride in aqueous medium (Bunton & Fendler, 1967), and the reaction of acetyl chloride with $(C_2H_5)_4NF$/acetic acid (Emsley et al., 1988).

We have employed FTIR spectroscopy in order to determine whether acyl fluorides are formed on mixing TAAF and acid anhydrides (ethanoic- or hexanoic anhydride) in DMSO at room temperature. In Fig. 1, we concentrate on the 1600–2600 cm^{-1} spectral region; the whole spectra are shown in Fig. SM-2. The solvent and TAAF solution in DMSO show no characteristic absorption bands in this spectral region. The anhydrides show the characteristic asymmetric and symmetric ($\tilde{\nu}_{C=O}$) stretching bands at 1822, 1742 (Fig. 1a) and 1813, 1742 cm^{-1} (Fig. 1e), for ethanoic- and hexanoic anhydride, respectively. Fig. 1b–d shows the $\tilde{\nu}_{C=O}$ region of acetic anhydride after its mixing with TAAF; likewise, Fig. 1f–h shows the corresponding spectra for hexanoic anhydride. For both sets of spectra, mixing of the anhydride with TAAF solution has resulted in the *immediate appearance* of new peaks at higher frequencies, namely, 1843 cm^{-1} (ethanoic) and 1838 cm^{-1} (hexanoic), whose intensity decrease as a function of time. As given elsewhere,

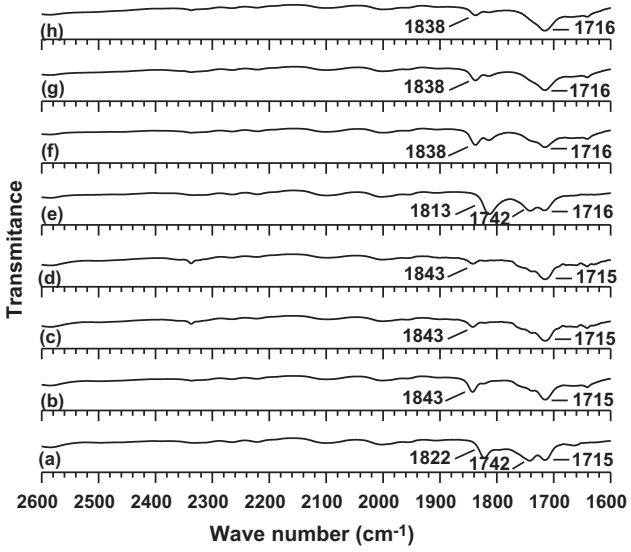
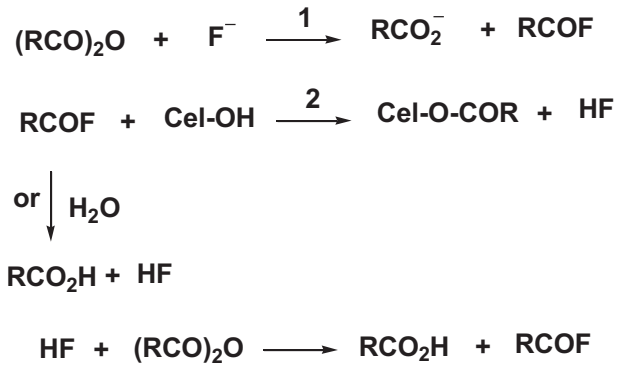


Fig. 1. Expanded IR spectra of the 2600–1600 cm^{-1} region, collected for (a) ethanoic anhydride and (e) hexanoic anhydride, both in DMSO. Parts (b–d) and (f–h) refer to the spectra of mixtures of TAAF plus ethanoic, and hexanoic anhydride, respectively. Each set refers to the spectra after *ca.* 5 min, 1 h and 2 h, respectively.

these new peaks can be attributed to the formation of RCOF, where R═CH_3 or C_4H_9 (Ramsey & Ladd, 1968), according to the following general reaction:

$$RCOOCOR + TAAF \rightarrow RCOF + TAAO_2CR$$

Some points are worth mentioning regarding the role of TAAF: (i) the IR experiments have been carried out at room temperature because of the low bp of acetyl fluoride, 20 °C (Olah & Kuhn, 1961); (ii) no biopolymer was dissolved in order to avoid the scattering of IR-radiation from the cellulose/TAAF–DMSO solution; (iii) it is plausible to argue that the OH groups of cellulose "solvate" the fluoride ion hence, in principle, decrease its nucleophilicity. Nevertheless, we think that this intermediate forms during the acylation of cellulose, because the production of RCOF has been detected in protic solvents, e.g., aqueous dioxane (Bunton & Fendler, 1967), and acetic acid (Emsley et al., 1988). That is, the F^- in protic media is still nucleophilic enough to form RCOF, at least from reactive derivative of carboxylic acids, e.g., acyl chlorides and acid anhydrides. Therefore, we suggest that TAAF, and probably TBAF are not spectators, their use lead to the formation of RCOF. The latter may suffer hydrolysis or react with cellulose, as illustrated in Scheme 5, especially when its bp is not low, e.g., C_3H_7COF (bp = 69 °C; Olah & Kuhn, 1961), and $C_5H_{11}COF$ (bp = 122 °C; Olah & Kuhn, 1961). The fraction of the ester formed via the RCOF route is, however, open to question in view of the reported lower reactivity of acyl fluorides, relative to other acyl halides, e.g., in acyl-transfer (Kivinen, 1972; Swain & Scott, 1953), and Friedel–Crafts reactions (Yamasi, 1961).



Scheme 5. Proposed mechanism for the acylation of cellulose that was obtained at least in part by means of acyl fluoride intermediate, as well as the hydrolysis of the latter.

Because we have not detected any attack of HF on the reaction flasks employed in the acylation experiments, we have included the last equation in Scheme 5, where any HF produced is consumed in producing more RCOF (Emsley et al., 1988). It is also plausible that a part of HF is strongly associated with the dissolved biopolymer (Oestlund et al., 2009).

4. Conclusions

The use of the solvent system TAAF·H_2O/DMSO is convenient for cellulose dissolution/derivatization. It readily dissolves MCC and fibrous celluloses, the solubilized bioploymer can be readily derivatized, e.g., into carboxylic esters and mixed esters. Several mechanistic aspects of this system have been investigated. Thus, TAAF in DMSO is not subjected to degradation by the ylide pathway; longer acylation reaction times should be avoided because they lead to fluoride ion-mediated ester hydrolysis, i.e., to products of low DS. The results of IR spectroscopy have indicated the intermediate formation acyl fluorides, i.e., TAAF has two roles, cellulose dissolution, and production of a potential acylating agent, RCOF.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2011.06.051.

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