Successful Application of an Ionic Liquid Carrying the Fluoride Counter-ion in Biomacromolecular Chemistry: Microwave-Assisted Acylation of Cellulose in the Presence of 1-Allyl-3-methylimidazolium Fluoride/DMSO Mixtures[a]

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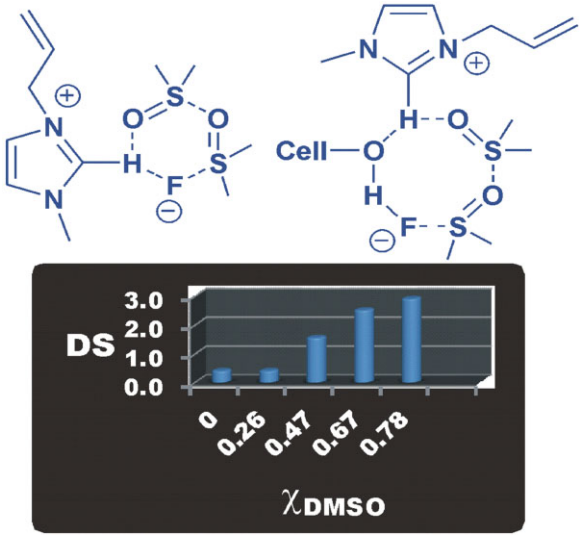
The use of ionic liquids with fluoride anion (IL-F) is challenging because of side reactions. Neat 1-allyl-3-methylimidazolium fluoride (AlMeImF) is used as a solvent in microwave-assisted acylation of cellulose. The results are disappointing due to side reactions in the IL proper, and F^--mediated hydrolysis of the produced ester. A dramatic improvement is observed, when AlMeImF/DMSO mixture is employed. The results are comparable to those obtained when pure 1-allyl-3-methylimidazolium chloride is employed. FTIR spectroscopy shows that dissolving a carboxylic acid anhydride in IL-F leads to the formation of acyl fluoride. Thus ILs are far from being "spectator" solvents. The new approach (use of IL-F/DMSO) is attractive because of its efficiency, low cost, and applicability to the derivatization of any polymer.



1. Introduction

Cellulose is the most abundant biopolymer; it is the source of many important derivatives, including esters and ethers that are employed in diverse applications (fibers, films, membranes, etc.). Cellulose-containing biomass is being intensely investigated as raw material for the production of bioethanol,[1,2] and other important chemicals.[3]

The strong inter- and intra-molecular hydrogen-bonding within the biopolymer is responsible for its semi-crystalline structure.[4–6] Cellulose dissolution, needed for derivatization under homogeneous conditions, requires disruption of this hydrogen-bonding network. Combinations of strong electrolytes and dipolar aprotic solvents, e.g., LiCl/*N*,*N*-dimethylacetamide and quaternary ammonium fluoride hydrates ($R_4NF \cdot xH_2O$) in DMSO have been successfully

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[a] **Supporting Information** for this article is available from the Wiley Online Library or from the author.

DOI: 10.1002/mabi.201200296

employed as media for cellulose dissolution and subsequent derivatization.[7–12]

Recently, ionic liquids (ILs), in particular those based on imidazole have attracted much attention as solvents for chemical reactions, including derivatization of several biopolymers under homogeneous reaction conditions.[6,13–15] There are several reasons behind this intense interest: ILs are composed of ions, so that no additional electrolyte, e.g., LiCl, is required for biopolymer dissolution; they are polar, chemically and thermally stable, and possess extremely low vapor pressure, a property that enhances process safety; their properties can be ''tailored'' to the researcher's needs by a judicious choice of the constituent ions.[16–20]

An important mechanism for cellulose dissolution involves hydrogen-bonding between the hydroxyl groups of the anhydroglucose units (AGUs), and the counter-ion of the IL.[6,21,22] Consequently, cellulose dissolution is largely dependent on the basicity of the anion; chloride, acetate, formate, and dialkylphosphate have been successfully employed.[6,13] The structure of the cation also plays a role, e.g., imidazole-based ILs with side-chains carrying heteroatoms (oxygen) dissolve cellulose better than those with saturated side-chains, although exceptions are known.[6,13,17,23–27] In this regard, the fluoride counter-ion, being small and of higher charge-density is expected to be the best member among the halogen series. A literature survey shows only few reports on the use of ILs with fluoride counter-ion, LI-Fs, for the dissolution of cellulose,[18,28,29] and, to our knowledge, none on the derivatization of the dissolved biopolymer. Several reasons can be advanced in order to explain this obvious gap.

1.1. Unavailability of the Starting Materials

Many organic fluorides, the starting materials for the syntheses of LI-Fs, are not commercially available. Therefore, the synthetic schemes for obtaining these (second generation) IL-Fs involve the synthesis of another IL-halide, followed by either ion-exchange or the use of (expensive) AgF.

1.2. Side Reactions in the IL-F Proper

In principle, there exists the possibility of several F^--mediated side-reactions, including abstraction of the relatively acidic C2-*H*, or other hydrogens of the imidazolium moiety,[30–34] elimination reactions involving the aliphatic side chain via Hoffman degradation, or an ylide mechanism, akin to the E1cB counterpart, except that the species produced by proton abstraction is a zwitterion.[35–38]

1.3. Fluoride-Ion-Mediated Side Reactions

Another possible side reaction, common to esterification in $R_4NF \cdot xH_2O$/dipolar aprotic solvents is F^--mediated ester hydrolysis, as observed for benzoates-,[39] and cellulose esters.[40]

In the present work, we have synthesized the IL 1-allyl-3-methylimidazolium fluoride, AlMeImF, and used it as solvent for the (homogeneous) acylation of cellulose by carboxylic acid anhydrides. The results were disappointing in terms of the ester degree of substitution (DS). We have attributed this result to side reactions, and raised the following questions: (1) What are the side reactions in case of this IL-F? (2) Is it possible to eliminate/attenuate them, so that the high electronegativity of the fluoride ion can be advantageously exploited for cellulose dissolution/derivatization? (3) What is the efficiency of AlMeImF as compared with that of the (extensively employed) 1-allyl-3-methylimidazolium chloride, AlMeImCl?

Our preliminary results have shown that neat AlMeImF is inferior to AlMeImCl. Surprisingly, however, addition of DMSO to the former not only solved the problem of low efficiency, but also led to the use of much less IL. In fact, we used AlMeImF as an ''electrolyte'' in DMSO, akin to others employed, e.g., LiCl, or $R_4NF \cdot xH_2O$. Thus the extra labor in the synthesis of this IL-F (ion-exchange) is more than compensated for by the higher efficiency of the resulting solvent system. Acylation of microcrystalline-, or eucalyptus cellulose in AlMeImF/DMSO yielded cellulose carboxylic esters with DS comparable to that obtained with neat AlMeImCl. In contrast to AlMeImF, dilution of the corresponding chloride with DMSO yielded cellulose acetates with lower DS.

2. Experimental Section

Notes: (i) As shown below, we have employed two samples of IL-F: one obtained without addition of DMSO; the other obtained by adding this molecular solvent to methanolic AlMeImF solution, before evaporation of the alcohol. These will be referred to as AlMeImF; AlMeImF/DMSO, respectively; (ii) the composition of AlMeImF/DMSO solution is given on the mole fraction scale; e.g., $AlMeImF_{0.22}/DMSO_{0.78}$ refers to a solution where the mole fractions are 0.22 and 0.78, for AlMeImF and DMSO, respectively.

2.1. Materials

The reagents were purchased from Acros, Aldrich, or Merck and were purified, where required, as described elsewhere.[41] Microcrystalline cellulose (MCC); Avicel PH 101 was from FMC (Philadelphia; viscosimetric degree of polymerization, $\overline{DP}_v = 175$). Eucalyptus sheets (Lwarcel Cellulose and Paper Co., São Paulo) were cut into stripes, grounded, sieved (100–200 mesh) and then mercerized by treatment with NaOH under reducing conditions, as given elsewhere; $\overline{DP}_v = 965$.[27]

2.2. Equipment

The value of $\overline{DP}_v$ was determined by using shear-dilution Cannon-Fenske viscosimeter (Schott), inserted in Schott AVS 360 automatic viscosity determination equipment. ^{1}H and ^{19}F NMR spectra were recorded with Varian Innova-300 spectrometer (300 MHz for ^{1}H); IR spectra were recorded with Bruker Vector-22 Fourier transform infrared (FTIR) spectrophotometer.

2.3. Material Characterization

The DS of cellulose carboxylic esters was determined either by the solvatochromic indicator method;[42] or by titration;[43] the results of both methods agree within ± 0.05. $\overline{DP}_v$ was determined (25 °C) from the intrinsic viscosity of cellulose solution in CUEN/water (1:1 v/v) according to the recommended procedure.[44]

2.4. Procedures for Spectroscopic Analyses

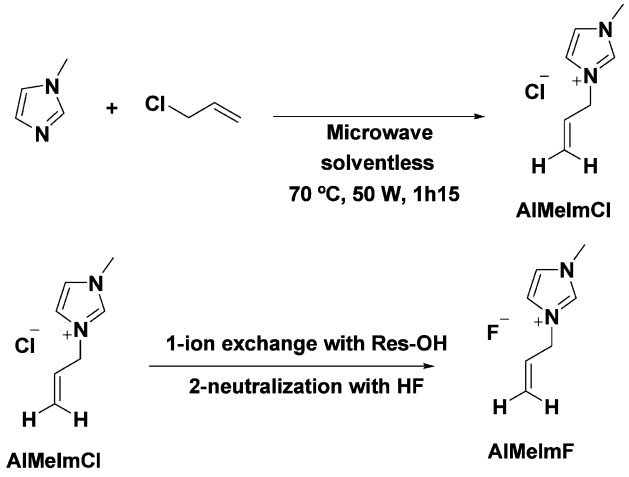
For ^{1}H NMR measurements, the sample solution in DMSO-d_6 was prepared ca. 30 min before the analysis; TMS was employed as internal reference; ^{19}F NMR chemical shifts were calculated relative to an external reference, 1 wt.-% trifluoroacetic acid solution in DMSO-d_6, contained in a Wilmad-Labglass 516-I-3 coaxial-tube. The IR spectra were recorded for the samples diluted with DMSO, by using 0.025 mm CaF_2 cell; 64 scans were added at 0.5 cm^{-1} digital resolution.

2.5. Synthesis of 1-Allyl-3-methylimidazolium Fluoride in the Absence of DMSO

The synthesis was carried out as shown in Scheme 1.

2.5.1. Synthesis of AlMeImCl

A mixture of 1-methylimidazol (20 mL, 0.25 mol) and allyl chloride (22.8 mL, 0.275 mol) was heated in an MW apparatus (Discover DU-8316, CEM) under the following conditions: MW-power, 50 W; reaction temperature, 70 °C; time, 75 min. Ethyl acetate (100 mL) was then added; the mixture stirred for 10 min; cooled in dry ice/ethanol bath (IL-Cl solidification), the supernatant discarded; this procedure was repeated at least three more times. The product was dissolved in methanol (80 mL) and stirred overnight with activated carbon (5 g). After filtration, the methanol was removed by heating the IL for ca. 4 h, 2 mmHg, 60 °C. The product is light yellowish-colored liquid that solidifies very slowly on standing (see part A of Figure S1; Figure S1 of Supporting Information); yield = 90%. The ^{1}H NMR spectrum of AlMeImCl (see Figure S2 of Supporting Information) agrees with literature data.[45–47]



Scheme 1. The three steps of the synthesis of AlMeImF: the reaction of 1-methylimidazole with allyl chloride; ($Cl^- \rightarrow OH^-$) ion-exchange; the neutralization of the hydroxide counterpart IL with HF.

2.5.2. Cl^-/OH^- Ion Exchange and Neutralization of AlMeImOH with HF

The counter-ion of the IL was converted into the corresponding hydroxide by ion exchange on a macro-porous resin (Purolite SGA55OOH, 1.10 equiv. OH^-/L), as follows: 1 L of a methanolic solution of AlMeImCl (0.25 mol) was passed through a glass column containing the resin (400 mL). The completeness of the (Cl^-/OH^-) ion-exchange was checked by treating a sample of the eluent 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. The methanol was removed by evaporation; the pressure was gradually reduced from 200 to 10 mmHg at 50 °C, then to 2 mmHg, at 60 °C for ca. 4 h. A dark amber-colored liquid was obtained, see Figure S1B of Supporting Information. Figure S3 of Supporting Information shows the ^{1}H NMR spectrum of the product, along with peak attribution of AlMeImF.

Because of the dark color of the IL-F produced (Figure S1-B of Supporting Information), methanol evaporation has also been carried out either at room temperature at 2 mmHg, or in the presence of propyl 3,4,5-trihydroxybenzoate (propyl gallate; 3 mol-% with respect to IL-F), at 60 °C for ca. 4 h, at 2 mmHg.

2.6. Synthesis of 1-Allyl-3-methylimidazolium Fluoride with Addition of DMSO

AlMeImF was obtained as given above (see Section 2.5); DMSO was added before the evaporation of methanol from the IL-F solution, i.e., after its neutralization with HF.[48] During this step, some DMSO was removed along with methanol (≤10%, by comparing the initial and final masses). The exact concentration of AlMeImF in DMSO was calculated by ^{19}F NMR spectroscopy, by using 3-nitro-α,α,α-trifluorotoluene as an internal reference. For comparison, AlMeImCl/DMSO was also prepared, but DMSO was added after the evaporation of methanol from the IL-Cl solution.

2.7. Determination of the Stability of AlMeImCl, AlMeImF, and AlMeImF/DMSO

2.7.1. By Employing ^{1}H NMR

A methanolic solution containing equimolar quantities of AlMeImCl and benzaldehyde (0.11 mol) was prepared; methanol was then evaporated as described in the synthesis of AlMeImF (pressure reduced from 200 to 10 mmHg at 50 °C, then at 2 mmHg,

60 °C for ca. 4 h); the resulting sample was analyzed by ^{1}H NMR (DMSO-d_6). The same procedure was employed for AlMeImF, and AlMeImF/DMSO-d_6; deuterated solvent was employed instead of $(CH_3)_2SO$.

2.7.2. By Employing FTIR

Four solutions in DMSO, containing the same concentration, 0.43 mol · L^{-1}, were prepared: (A) benzaldehyde, (B) AlMeImF, (C) AlMeImF/DMSO, and (D) AlMeImCl. Equal volumes of solutions A plus B; A plus C; A plus D were added to glass vials, equipped with screw-caps. The latter were tightly closed, the components mixed, and kept at room temperature. The IR spectra of each solution were recorded right after mixing, and after 5, 24, 48, and 72 h. The area of the benzaldehyde $\upsilon_{C=O}$ peak at 1 698 cm^{-1} was calculated from the 1 720 to 1 680 cm^{-1} section of the spectrum, by employing a commercial software (Grams/32; version 5, Galactic Industries, Salem).

2.8. Effect of Heating Cellulose Triethanoate with AlMeImF or AlMeImF/DMSO on the Degree of Substitution of the Ester

Solutions of commercial cellulose triethanoate (CA 398-6; DS = 2.7; Eastman) were prepared by mixing the ester (0.55 g) with 11 g of each of the following in one-neck round-bottom flasks: AlMeImF; AlMeImF/DMSO; or AlMeImCl. Using MW-heating (30 W), each solution was heated at 80 °C, for 3 h, under mechanical stirring (model RW 20; IKA Labortechnik; 570 rpm). The resulting solution was added to ethanol (400 mL); the suspension was stirred for 30–60 min; the precipitated solid was centrifuged at 3 500 g (IEC Centra 244 MP4R). This procedure was repeated three more times; the product was dried under reduced pressure at 50–60 °C, for 48 h, and its DS determined.

2.9. Investigation of IL-F/Acid Anhydride Mixtures by FTIR

In glass vials provided with screw-caps, solutions of the following, each 0.43 M in DMSO, were prepared: (A) AlMeImF/DMSO; (B) ethanoic anhydride; (C) hexanoic anhydride. Mixtures were then prepared by adding equal volumes of (A) plus (B), and (A) plus (C). For each mixture, the IR spectra were recorded right after mixing, 5 h, and 24 h.

2.10. Dissolution and Acylation of Cellulose in AlMeImF and AlMeImF/DMSO

Cellulose (0.50 g) was added to 10 g AlMeImF, AlMeImF/DMSO, AlMeImCl, or AlMeImCl/DMSO. Each mixture was mechanically stirred (570 rpm) at 80 °C, for 20–40 min, by applying MW-radiation (30 W). Cellulose dissolution was followed visually by employing a lamp placed behind the reaction flask. MCC and eucalyptus cellulose dissolve readily in AlMeImCl or AlMeImCl/DMSO; resulting in clear solutions. On the other hand, solutions of MCC in AlMeImF or AlMeImF/DMSO were translucent; addition of the carboxylic acid anhydride resulted in the formation of clear solutions, fast for MCC and slow for fibrous cellulose.

The solution was kept under the above-mentioned conditions during the required length of time, vide infra. The resultant was added to ethanol (400 mL), stirred for 30–60 min, at ca. 60 °C, and the precipitated cellulose ester centrifuged at 3 500 g. This washing procedure was repeated three more times; the product was dried under reduced pressure at 50–60 °C, for 48 h, and its DS determined.

3. Results and Discussion

The Results and Discussion part is organized as follows: (i) The results of cellulose acylation in neat AlMeImF are shown; (ii) Possible side reactions that occur in this IL are investigated; (iii) A solution is given for the problem of side reactions; (iv) Results of acylation of celluloses in AlMeImF/DMSO are listed and compared with those for neat AlMeImCl and AlMeImCl/DMSO; (v) Nature of the acylating agent(s) is discussed; (vi) A tentative explanation for the role of DMSO is given.

3.1. Cellulose Acylation in Neat AlMeImF

After dissolution of MCC in neat AlmeImF, or AlMeImCl (the latter for comparison), ethanoic anhydride was added and the MW-assisted reaction was carried out at 80 °C and 30 W, for 1–6 h. Table 1 shows the reaction conditions and values of the DS obtained. Relative to AlMeImCl, the acetylation reaction in IL-F is inefficient in terms of the DS obtained. As will be discussed below, attempts to solve this problem (entries 6 and 7 of Table 1) did not change much the DS obtained.

3.2. Investigation of the Possible Side Reactions that Occur During the Synthesis of AlMeImF

We have raised two possible reaction pathways that can contribute to the disappointing results shown in Table 1, namely: (1) fluoride-ion mediated de-acylation, akin to that observed for benzoate esters in $(C_4H_9)_4NF \cdot 3H_2O$ (TBAF)/DMSO,[39] and cellulose triethanoate in tetraallylammonium fluoride (TAAF) · H_2O/DMSO;[40] (2) side reactions occurring in the IL-F proper.

With regard to (1), the following experiment has been carried out: A commercial sample of cellulose triethanoate (DS = 2.7) was dissolved in neat AlMeImF or AlMeImCl; each solution was stirred at 80 °C (MW; 30 W); the DS of the ester was determined after 3 h. The results obtained were as follows: in AlMeImCl, DS = 2.6; in AlMeImF, DS = 1.1. Therefore, F^--mediated deacylation occurs in neat IL-F. The mechanistic possibilities for this reaction include: fluoride ion-mediated ester hydrolysis, where (F^-) is acting either as a general base (a), or nucleophile (b); F^--mediated deacylation due to side reaction that generate an ylide (c), or

Table 1. Results of the acetylation of MCC in AlMeImF, or AlMeImCl, for comparison.[a)]

Entry	Solvent/reaction medium	Ac_2O/AGU[b)]	Reaction time [h]	DS of the product
1	AlMeImF	3	1	0.2
2	AlMeImF	6	1	0.3
3	AlMeImF	6	2	0.3
4	AlMeImF	6	3	0.4
5	AlMeImF	6	6	0.2
6	AlMeImF[c)]	6	3	0.4
7	AlMeImF[d)]	6	3	0.4
8	AlMeImCl	3	3	0.95
9	AlMeImCl	6	3	2.95

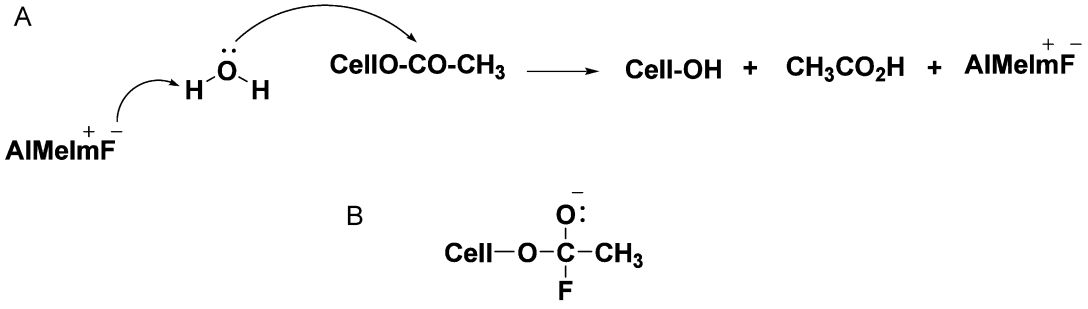
[a)]Microwave-assisted acetylation (30 W, 80 °C); [b)]molar ratio between ethanoic anhydride (AC_2O) and AGU; [c)]the methanolic solution was evaporated at room temperature, under reduced pressure; [d)]propyl gallate (3 mol-%/mol AlMeImF) was added prior to evaporation of methanol.

an anion (d). Recently, we have shown that cellulose acetate hydrolysis occurs in TAAF/DMSO, where no F^--mediated elimination occurs.[40] Therefore, (a) or (b) may occur concomitant with (c) or (d).

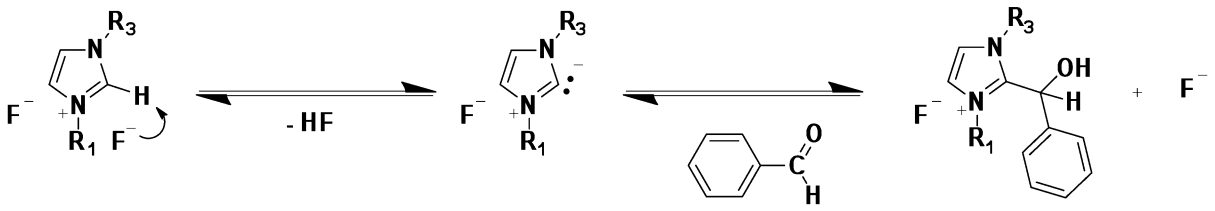
Scheme 2 addresses the mechanistic possibilities (a) and (b). Part (A) of this scheme shows that the counter-ion of the IL is promoting ester hydrolysis by acting as a general base for the attack of water. The source of water may be the biopolymer itself (not dried), or the (hygroscopic) IL-F. Part (B) of the same scheme shows the intermediate formed (via attack of F^- on the ester C=O group) if the fluoride ion were acting as a nucleophile. This alternative is most certainly not operative because F^- is a better leaving group from the tetrahedral intermediate than (Cell-O^-).

Alternative (c) involves the attack on the ester C=O group by an ylide, formed via F^--mediated abstraction of C2-*H* of the imidazolium ring, followed by elimination of (Cell-O^-). The mechanism of formation of this ylide is shown in Scheme 3 below. Recently, it has been postulated that deaylation of cellulose ester by TBAF/DMSO occurs via F^--mediated elimination of *H*-CH_2CO-OCell, followed by deacetylation, due to the formation of ketene (CH_2=C=O), alternative (d).[49] Although further discussion of these possibilities is outside the scope of the present work, all are based on the high basicity of F^- in DMSO.

Probing the nature and extent of side reactions occurring in the IL proper is important per se, and because this bears on the potential use of IL-Fs as solvents for chemical reactions, including those of cellulose and other biopolymers. AlMeImF was synthesized from AlMeImCl via ($Cl^- \rightarrow OH^-$) anion-exchange, followed by neutralization with HF, and methanol removal by two-step evaporation; vide Experimental. As shown in Figure S1 of Supporting Information both ILs differ in color; AlMeImCl is light-, whereas AlMeImF is dark-amber. A more fundamental difference, however, is the evolution of gas bubbles during



Scheme 2. Part (A) shows the fluoride ion-mediated cellulose ethanoate hydrolysis through a general base catalyzed attack of water on the ester acyl group. Part (B) depicts the structure of the tetrahedral intermediate formed by nucleophilic attack of (F^-) on the ester, if the reaction involves nucleophilic catalysis.



Scheme 3. Suggested mechanism for the reactions occurring in the IL-F/aldehyde mixture. The initial step is F^--mediated abstraction of C2-*H* of the imidazolium ring, followed by nucleophilic addition of the ylide formed to the carbonyl group of benzaldehyde.

the evaporation of methanol under reduced pressure (at 2 mmHg). This is observed only for AlMeImF and may be taken to indicate side reactions, an assumption corroborated by comparing the ^{1}H NMR spectra of both ILs; AlMeImF has several peaks not present in the spectrum of the corresponding chloride (Figure S2 and S3 of Supporting Information).

Two strategies have been attempted in order to eliminate/attenuate the above-mentioned problem: use of lower evaporation temperature; addition of an efficient antioxidant. Although methanol evaporation at room temperature has resulted in lighter-color product (orange), the corresponding ^{1}H NMR spectrum still showed additional peaks (spectrum not shown). Because propyl gallate is an efficient inhibitor for both homolytic and heterolytic side reactions,[50] we tested the effect of its addition before methanol evaporation. Again, the IL-F produced was dark-colored (probably due to the oxidation of propyl gallate);[50] evolution of gas has been observed during the evaporation of methanol; ^{1}H NMR spectrum showed several additional peaks (spectrum not shown). In summary, both procedures did not solve the problem.

The occurrence of side reactions can be explained on the bases of abstraction of the relatively acidic C2-*H* of the imidazolium moiety by the fluoride ion (F^- is isoelectronic with OH^-).[30–32,51] In order to test our assumption (hydrogen atom abstraction), evaporation of methanol from AlMeImF solution (no DMSO added) has been carried out in the presence of added benzaldehyde. For comparison, the same experiment was repeated with AlMeImCl. The idea of this experiment is to "trap" the intermediate ylide formed by abstraction of C2-*H* of the imidazolium ring as a stable addition product to benzaldehyde, as shown in Scheme 3. This approach is similar to that employed for probing the effect of a base (3-hydroxyquinuclidine) on 1-butyl-3-methylimidazolium chloride, where the aldehyde C*H*=O peak at 10.0 ppm has been replaced by a peak at 6.35 ppm.[30]

First, we discuss the experiment of AlMeImCl. As can be seen from Figure 1, the ^{1}H NMR spectrum obtained for the AlMeImCl/benzaldehyde mixture after methanol evaporation is simply the sum of the peaks of both components. In particular, there is no peak at ca. 6.3 ppm, attributed to the AlMeImCl-derived ylide-aldehyde addition product. Figure 2 shows the same result for the IL-F. The salient feature is the presence of several additional peaks (as compared with Figure 1), in particular the singlet at ca. 6.3 ppm. This confirms the formation, and subsequent addition of the above-mentioned ylide to benzaldehyde. The decrease in the intensity of the latter peak after complete evaporation of methanol (compare the whole spectrum and the inset in Figure 2) is a consequence of the reversibility of the two reactions (H-abstraction and addition to $C_6H_5CH{=}O$), as shown in Scheme 3, and discussed elsewhere.[30]

FTIR is a powerful tool to probe the formation of the above-mentioned addition product, because the $\upsilon_{C=O}$ band of the aldehyde is strong and symmetrical. Therefore, the area of this peak has been followed as a function of time; the results are shown in Figure 3.

As part (A) of Figure 3 clearly shows, there is practically no change in the area of the $\upsilon_{C=O}$ band of the benzaldehyde/AlMeImCl mixture as a function of time. This indicates that the IL-Cl is stable under these experimental conditions. On the other hand, the peak area for the corresponding AlMeImF (part B) decreased to 38% of its original value after 5 h and changed very little afterword; most probably due to the reversibility of above-indicated (ylide-benzaldehyde) addition reaction. The results of part (C) will be discussed later.

In summary, ^{1}H NMR and FTIR results of the trapping experiment corroborate that the side reaction in case of AlMeImF is F^--mediated hydrogen abstraction from the substituted imidazolium ring.

3.3. Solution of the Problem of Side Reactions

The following question now arises: can the elimination side reaction be stopped/suppressed by addition of DMSO before methanol evaporation? Our reasoning rests on the ability of DMSO to associate with ILs whose counter-ions contains fluorine, e.g., the 1-butyl-3-methylimidazolium- and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate.[52] We have reasoned that DMSO is especially suited for the job, because: (i) solvation of (F^-), if it occurs, should

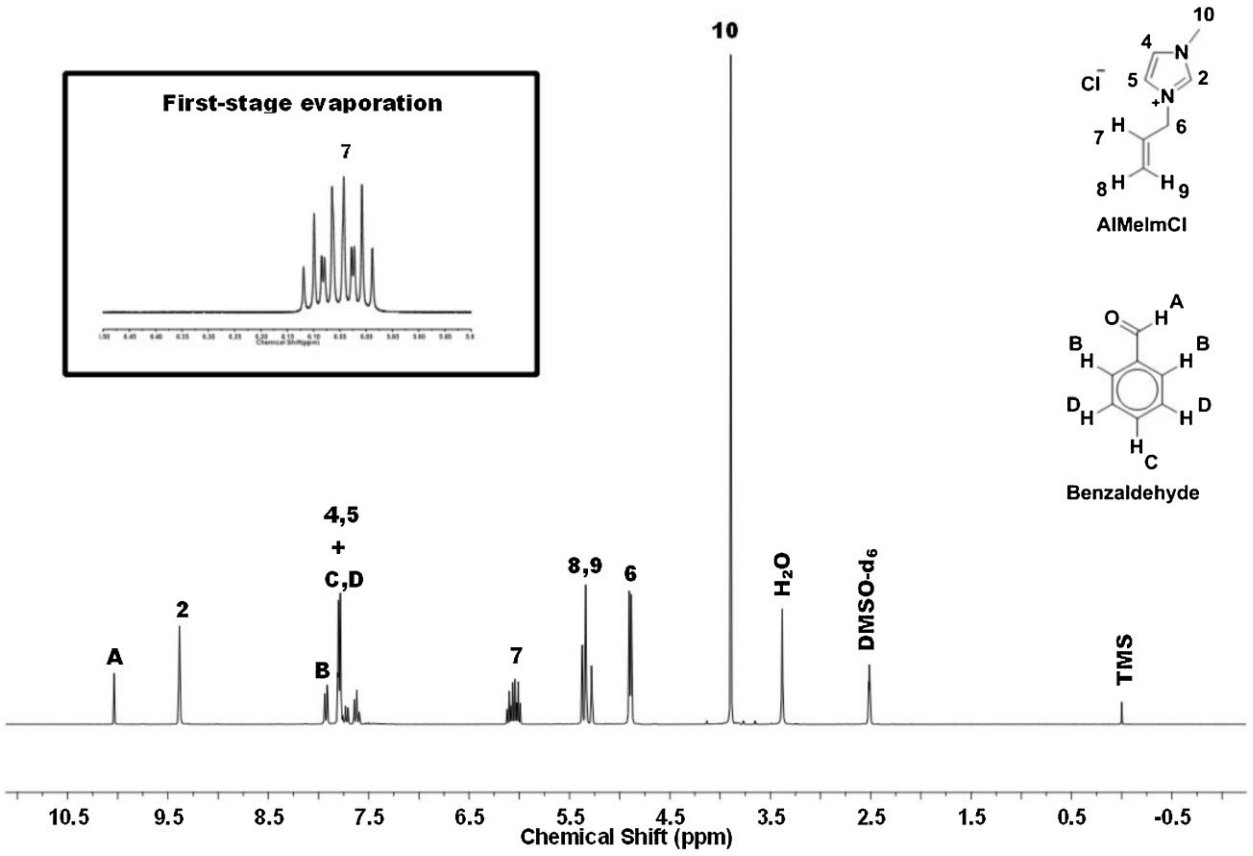


Figure 1. ^{1}H NMR spectrum for the mixture of AlMeImCl and benzaldehyde after a two-stage methanol evaporation (200–10 mm Hg, 50 °C; 2 mmHg, for ca. 4 h, at 60 °C). The region 6.50–5.80 ppm is expanded in the inset; it refers to the same mixture after the first stage of methanol evaporation. There is no peak at ca. 6.3 ppm, attributed to the IL-Cl derived ylide-aldehyde addition product.

decrease its basicity, hence stop/suppress the side reactions; (ii) being a strongly dipolar solvent, DMSO should form hydrogen-bond with the C2-*H* of the imidazolium ring, hence decrease its interaction with the (F^-); (iii) the concomitant removal of DMSO during methanol evaporation should be small, because of its high b.p., 189 °C; (iv) cellulose dissolution in the resulting IL-F/DMSO should be favorable because of the high capacity of the molecular solvent in causing biopolymer swelling (DMSO ranks second only to water).[53,54]

Although part (C) of Figure S1 of Supporting Information shows that AlMeImF/DMSO is still dark-colored, its ^{1}H NMR spectrum (Figure S4 of Supporting Information) shows fewer additional peaks; no gas evolution has been observed during methanol evaporation, provided that the mole fraction of DMSO in the mixture, χ_{DMSO} is $\geq$0.5. Part (C) of Figure 3 shows that the extent of ylide trapping has decreased noticeably after 5 h, from 62 to 20%, when DMSO has been added before alcohol evaporation. Additionally, the intensity of the singlet at ca. 6.3 ppm in the ^{1}H NMR spectrum (not shown) obtained for the AlMeImF/DMSO and benzaldehyde mixture is smaller than that shown in Figure 2 (for AlMeImF/benzaldehyde). Therefore, the addition of DMSO leads to suppression of H-abstraction reaction to a large extent, probably due to the AlMeImF-DMSO interactions, as depicted in Scheme 4.[21,52] The rationale for these structures will be discussed in Section 3.6; vi.

A clear indication that our expectation is valid can be reached by comparing the DS results analyzed for (commercial) cellulose triethanoate after treatment (80 °C; 30 W; 3 h) with ILs, point above (Section 3.2; ii): original sample, 2.70; AlMeImCl, 2.60; $AlMeImCl_{0.22}$/$DMSO_{0.78}$, 2.65; AlMeImF, 1.1; $AlMeImF_{0.22}$/$DMSO_{0.78}$, 2.5. That is, addition of DMSO also suppressed fluoride ion-mediated ester hydrolysis.

It is legitimate to suggest that the ion-exchange and neutralization steps, vide Experimental, could have been carried out in neat DMSO instead of methanol. To be successful/efficient, ion-exchange reactions are usually carried out in the laboratory by using relatively dilute solutions. Therefore, a large volume of DMSO would have

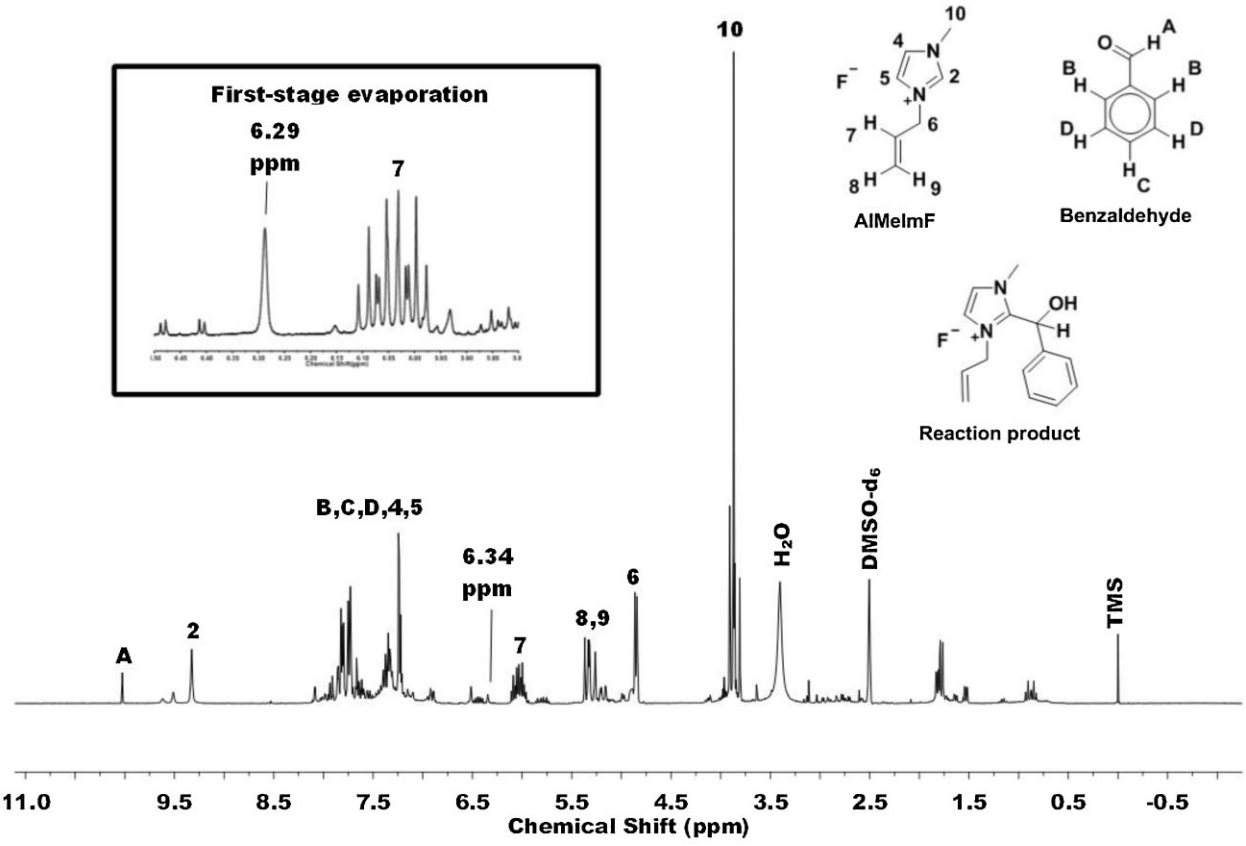


Figure 2. ^{1}H NMR spectrum for the mixture of AlMeImF and benzaldehyde after a two-stage methanol evaporation (200–10 mm Hg, 50 °C; 2 mmHg, for ca. 4 h, at 60 °C). The region 6.50–5.80 ppm is expanded in the inset; it refers to the same mixture after the first stage of methanol evaporation.

been needed; this excess should be partially evaporated in order to obtain IL-F/DMSO of the required composition. This procedure, however, would have been both energy intensive and expensive, in view of the large difference in the b.p. (65; 189 °C) and relative cost (1 and 3.3; ACS-grade solvents; prices for one liter) of methanol and DMSO, respectively.

3.4. Acylation of Celluloses in AlMeImF/DMSO and Comparison with the Reactions in AlMeImCl and AlMeImCl/DMSO

Acetylation of MCC was carried out in AlMeImF/DMSO as solvent; the results are shown in Figure 4 and Table 2. The DS values increase as a function of increasing χ_{DMSO} reaching 2.9 at $AlMeImF_{0.22}/DMSO_{0.78}$, which is equal to that of the reaction in neat AlMeImCl (2.95, Table 1), using only one third in mass of the IL. Despite the dark amber color of AlMeImF/DMSO solution, the color of cellulose acetate obtained is similar to that of the reaction in AlMeImCl (Figure S1 of Supporting Information).

AlMeImF/DMSO has also been successfully employed for the synthesis of other esters, butanoate and hexanoate, see Table 2. The dependence of DS on the anhydride employed is similar to that observed elsewhere, i.e., ethanoic ≈ hexanoic > butanoic.[19,55] As recently shown, this dependence of DS on the length of the acyl moiety of the anhydride is due to subtle changes in- and compensations of the enthalpy and entropy of activation.[56]

Acetylation of (fibrous) eucalyptus cellulose has also been successfully carried out in AlMeImF/DMSO, as shown in Table 2. The DS values of the acetates increase with increasing χ_{DMSO} in the mixture, similar to that observed for the acetylation of MCC. As expected, the DS value obtained for MCC is greater than that for eucalyptus (Table 2), due to differences in $\overline{DP}_v$ and, most certainly, in the accessibility of microcrystalline- and fibrous biopolymers.[57] As observed for MCC, the acetylation of fibrous cellulose in $AlMeImF_{0.22}/DMSO_{0.78}$ gave DS value equal to that in neat AlMeImCl. Finally, the efficiency of AlMeImF/DMSO relative to the corresponding AlMeImCl/DMSO is shown by the large difference in DS at the same χ_{DMSO}, Table 2.

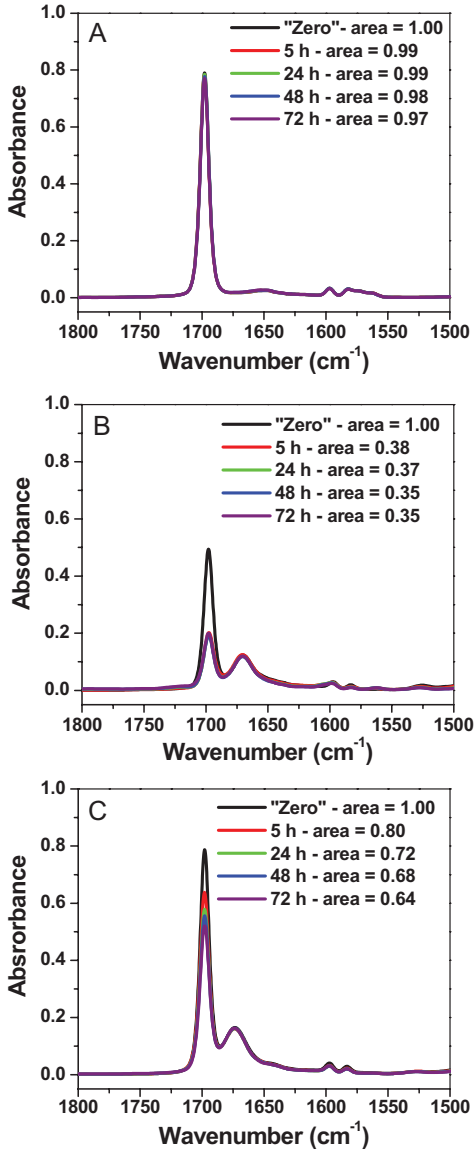
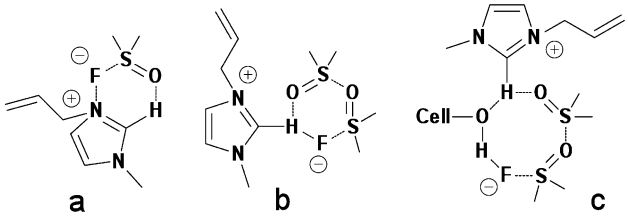


Figure 3. The 1800–1500 cm^{-1} region of the IR spectra of 1:1 molar mixtures of benzaldehyde and (A) AlMeImCl, (B) AlMeImF, (C) $AlMeImF_{0.22}/DMSO_{0.78}$ acquired after "zero", 5, 24, 48, and 72 h. Expanded region from 1800 to 1500 cm^{-1}.



Scheme 4. Representative "snap-shots" of the proposed interactions of AlMeImF with DMSO. Structure (a) shows one possibility for a six-member "ring" solvation of (F^-), involving DMSO, the positively charged nitrogen-, and C2-*H* of the imidazolium ring. The same ring size has been maintained in (b), but the stoichiometry DMSO/IL-F is 2:1. Structure (c) shows the cellulose/IL-F/DMSO interaction via an 8-member ring formation.

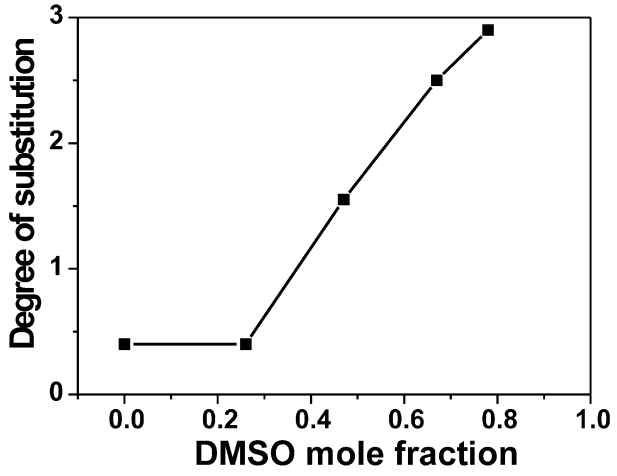


Figure 4. Dependence of the DS of cellulose acetate on the mole fraction of DMSO in the mixture of AlMeImF/DMSO. Experimental conditions: 3 h, 80 °C, 30 W, and Ac_2O/AGU molar ratio of 6; data for MCC.

3.5. Nature of the Acylating Agent: Detection of Acyl Fluoride Formation by FTIR

It is now recognized that as solvents, ILs are not always "spectators"; they may participate in the reaction.[58–60] This participation, in fact, is the base of the so-called task-specific ILs.[16] Is it possible that a fraction of the ester is produced via the reaction of cellulose with acyl fluoride, RCOF? In principle, the latter can be formed by the nucleophilic attack of the fluoride counter-ion on the anhydride, as shown by the reaction:

$$RCOOCOR + AlMeImF \rightarrow RCOF + AlMeImO_2CR$$

The above-raised question is based on the following facts: (F^-) is a powerful nucleophile, especially when it is desolvated;[61] the formation of acyl fluorides has been experimentally demonstrated in, e.g.: the preparation of perhalo-alkyl acrylate and methacrylate esters;[62] the hydrolysis of acetic anhydride in aqueous medium;[63] the reaction of acetyl chloride with TBAF/acetic acid;[64] the reaction of TAAF with carboxylic acid anhydrides in DMSO.[40]

We have employed FTIR in order to examine solutions of acid anhydrides (ethanoic- or hexanoic) in AlMeImF/DMSO, in absence (spectra not shown) and presence of cyclohexylmethanol, CHM. The latter carries a primary (OH) group and has been successfully employed as a model for the

Table 2. Results of acylation of MCC, or eucalyptus cellulose, in AlMeImF, AlMeImF/DMSO, AlMeImCl, and AlMeImCl/DMSO.[a)]

Solvent	Cellulose	Carboxylic anhydride	Ester DS
$AlMeImF_{0.74}/DMSO_{0.26}$ [b),c)]	MCC	Ethanoic	0.4
$AlMeImF_{0.53}/DMSO_{0.47}$ [b),c)]	MCC	Ethanoic	1.55
$AlMeImF_{0.33}/DMSO_{0.67}$ [b),c)]	MCC	Ethanoic	2.5
$AlMeImF_{0.22}/DMSO_{0.78}$ [b),c)]	MCC	Ethanoic	2.9
$AlMeImF_{0.33}/DMSO_{0.67}$ [c)]	MCC	Butanoic	2.1
$AlMeImF_{0.33}/DMSO_{0.67}$ [c)]	MCC	Hexanoic	2.65
$AlMeImF_{0.53}/DMSO_{0.47}$ [c)]	Eucalyptus	Ethanoic	1.1
$AlMeImF_{0.33}/DMSO_{0.67}$ [c)]	Eucalyptus	Ethanoic	1.7
$AlMeImF_{0.22}/DMSO_{0.78}$ [c)]	Eucalyptus	Ethanoic	2.1
AlMeImCl	Eucalyptus	Ethanoic	2.2
$AlMeImCl_{0.22}/DMSO_{0.78}$ [c)]	MCC	Ethanoic	1.2
$AlMeImCl_{0.22}/DMSO_{0.78}$ [c)]	Eucalyptus	Ethanoic	1.1

[a)]Experimental conditions: 3 h, 80 °C, 30 W, and carboxylic anhydride/AGU molar ratio of 6. Eucalyptus cellulose was mercerized; [b)]these data were plotted in Figure 4; [c)]the following are the weight- and mole-fractions employed for AlMeImF/DMSO: 0.84/0.16, 0.74/0.26; 0.67/0.33, 0.53/0.47; 0.47/0.53, 0.33/0.67; 0.34/0.66, 0.22/0.78. The corresponding values for AlMeImCl/DMSO are: 0.36/0.64, 0.22/0.78, respectively.

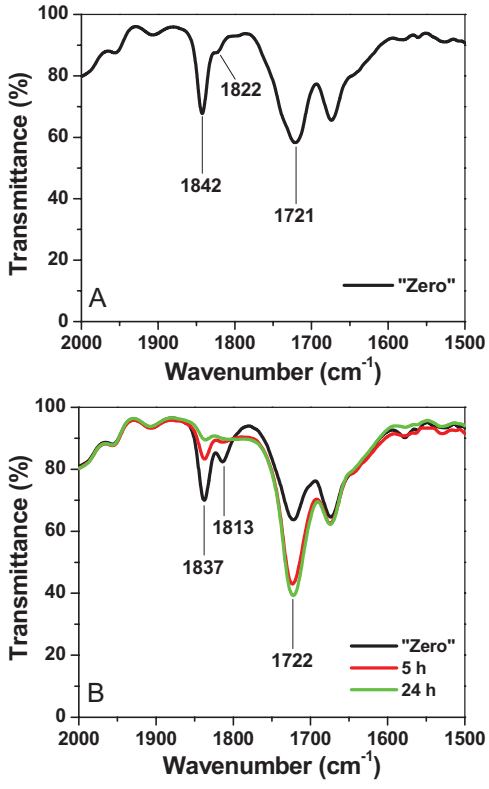


Figure 5. The 2 000–1 500 cm^{-1} IR spectral region of the mixtures: ($AlMeImF_{0.33}/DMSO_{0.67}$); ethanoic anhydride, and CHM right after mixing (A); $AlMeImF_{0.33}/DMSO_{0.67}$; hexanoic anhydride, and CHM (B) as a function of time.

C6-OH of the AGU.[56] Room temperature has been employed because of the volatility of CH_3COF, if it is formed, b.p. = 20 °C.[40,65]

As expected, the anhydrides show the characteristic asymmetric and symmetric C=O stretching vibrations at 1 822, 1 742, and 1 813, 1 742 cm^{-1}, for ethanoic- and hexanoic anhydride, respectively. The formation of acyl fluorides is observed right after mixing at 1 842 cm^{-1} (Figure 5A, CH_3COF), and 1 837 cm^{-1} (Figure 5B, $C_5H_{11}COF$), in agreement with literature values.[66] As shown in Figure 5B, as a function of time, the intensity of $\nu_{C=O}$ of RCOF decreased, and that of $\nu_{C=O}$ of $C_5H_{11}CO_2H$ (1 722 cm^{-1}) increased, probably due to the reaction with CHM and/or with adventitious water. Although it is known that acyl fluorides have lower reactivity, relative to other acyl halides, e.g., in acyl-transfer-,[67,68] and Friedel-Crafts reactions,[69] it is safe to assume that at least a part of the product is formed by reaction with RCOF.

3.6. A Tentative Explanation of the Role of DMSO

We offer tentative explanation for the suppression of the side reactions, and for the higher efficiency of IL-F/DMSO, as compared to its IL-Cl/DMSO counterpart. Efficient solvation of (F^-) of AlMeImF is expected to decrease its basicity, hence its tendency for ester hydrolysis and imidazolium C2-*H* elimination. Structures (a) and (b) of Scheme 4 are derived from the observation that DS increases noticeably at ca. $\chi_{DMSO} \geq 0.5$, corresponding to 1:1 IL-F-DMSO complex.

This solvation may occur via the formation of the relatively stable six-membered "ring", containing one-, or two DMSO molecules. Both show the hydrogen bonds formed between C2-$\underline{H}$•••O = S, and C2-$\underline{H}$•••F^-, in agreement with published data on IL-BF_4.[52,70,71] As shown elsewhere,[72] DMSO does not perturb noticeably the interactions between the ions of IL-Cl, e.g., 1-butyl-3-methylimidazolium chloride, BuMeImCl, so that ILs clusters persist, even at low concentration of the IL-Cl in this molecular solvent. This persistence may be deduced, indirectly, from the report that up to 15 wt.-% of DMSO has no apparent effect on the ability of BuMeImCl to dissolve polysaccharide-rich biomass.[72] This may be taken to indicate that the structure of this IL-Cl is not largely perturbed by DMSO. In fact, a clear solution of extensively swollen MCC in BuMeImCl/DMSO, χ_{DMSO} 0.92, was obtained by Rinaldi.[73] In summary, the IL-F interacts more strongly with the strongly dipolar DMSO than the corresponding IL-Cl, this leads to efficient solvation of strongly basic fluoride ion, and suppression of its capacity to induce the above-mentioned elimination reaction, and (general-base catalyzed) hydrolysis of the ester formed. Our results can be analyzed quantitatively in terms of the dependence of DS on, e.g., solvent basicity, dipolarity, and polarizability, as measured by solvatochromic probes.[20] This analysis, however, is not feasible at this stage; DS for the reaction in IL-F dissolved a group of dipolar aprotic solvents are necessary in order to obtain statistically significant correlations.

With regard to the higher efficiency of AlMeImF/DMSO, consider structure (c) of Scheme 4, that is derived from structure (b) by insertion of a cellulose molecule, leading to the formation of an 8-membered "ring". Structure (c), if it is formed, is expected to enhance not only the accessibility of cellulose, but also its reactivity due to partial weakening of Cell-O-$\underline{H}$, with concomitant increase in the nucleophilicity of Cell-$\underline{O}$-H. A possible support for structure (c) comes from the observation that the biopolymer solution in AlMeImF/DMSO turns clear only after addition of the acid anhydride (vide Experimental), i.e., when such cyclic, cellulose-containing structures may have started to become more soluble due to the acylation reaction proper. Because of the weaker IL-Cl-DMSO interactions, the formation of structure (c) may be less favorable, leading to the observed lower DS for cellulose acylation in AlMeImCl/DMSO, relative to the IL-F counterpart.

4. Conclusion

The use of AlMeImF for cellulose dissolution and subsequent derivatization is problematic due to the occurrence of F^--mediated side reactions. These include cellulose ester hydrolysis and abstraction of the relatively acidic C2-$\underline{H}$ of the imidazolium moiety. These side reactions have precluded the use of IL-Fs as media for chemical reactions, including the derivatization of cellulose and other biopolymers. In order to solve this problem, we have taken advantage of the relatively strong solvation of (F^-) by DMSO. This reduce C2-$\underline{H}$ abstraction by a factor of 2.1 (5 h, room temperature), turning acylation of cellulose feasible. It also suppresses general-base catalyzed ester hydrolysis. Equally important, however, is the fact the medium employed, $AlMeImF_{0.22}/DMSO_{0.78}$ is composed essentially of (relatively inexpensive) DMSO; the IL-F is acting as an electrolyte, akin to LiCl (in DMAC) and R_4NF.xhydrate (in DMSO). Therefore, the extra labor and cost involved in obtaining AlMeImF/DMSO is more than compensated for by using the IL-F as an electrolyte, not a solvent. These results make AlMeImF/DMSO a potential candidate for the dissolution/derivatization of other biopolymers, and for large-scale processing of biomass.

Acknowledgements: We thank the FAPESP (State of São Paulo Research Foundation) for financial support and a postdoctoral fellowship to R. Casarano; the CNPq (National Council for Scientific and Technological Research) for a productivity fellowship to O. A. El Seoud. We also thank Paulo A. R. Pires for the NMR analyses and Cezar Guizarro for his help. This work has been carried out within the frame of INCT-Catálise.

Received: August 11, 2012; Revised: October 9, 2012; Published online: January 9, 2013; DOI: 10.1002/mabi.201200296

Keywords: acyl fluorides; 1-allyl-3-methylimidazolium fluoride; biopolymer-(ionic liquid)-DMSO interactions; cellulose esterification

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