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Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201601830

Link to VoR: http://dx.doi.org/10.1002/cssc.201601830



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10.1002/cssc.201601830

Improving cellulose dissolution in ionic liquid by tuning the size of the ions: impact of the length of the alkyl chains in tetraalkylammonium carboxylate

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Abstract

20 ionic liquids based on tetraalkylammonium cations and carboxylate anions have been synthetized, characterized and tested for cellulose dissolution. The amount of cellulose dissolved in these ionic liquids is depending strongly on the size of the ions: from 0 to 22 wt% of cellulose can be dissolved at 90 °C. The best ionic liquids are the less viscous and these ammonium carboxylate based ionic liquids can dissolve as much as the imidazolium based ones. The viscosity of an ionic liquid can be decreased by the addition of DMSO as co-solvent. After addition of co-solvent, similar amount of cellulose per ions is reached for most ionic liquids. As observed by rheology, ionic liquids having the longest alkyl chains form a gel when high amount of cellulose is dissolved which limits drastically their potential. Molecular simulation and IR spectroscopy have also been used with the aim to understand how molecular interactions differ between efficient and inefficient ionic liquids.

Introduction

The objective of biorefinery is to transform renewable biomass into valuable fuels, chemicals and materials.^[1] One of the challenges which have to be overtaken before the industrialization of the biorefinery concept is the conversion of the biomass in a liquid state and in particular the dissolution of the cellulose.^[2] This step is difficult because of the strong hydrogen bond network (intra and intermolecular) as well as the hydrophobic interactions between the sheets of the crystalline form of this biopolymer. The dissolution of cellulose has been studied for over a century and several processes (like Viscose using CS₂ or Lyocell using 4-Methylmorpholine N-oxide (NMMO)) have proved their efficiency.^[3] However, the technologies developed so far have ecological or economical drawbacks (toxicity, recyclability). In 2002, it was published for the first time that ionic liquids could dissolve efficiently cellulose: up to 10 wt% of cellulose in a chloride based ionic liquid at 100 °C.^[4] Afterward, many research groups have studied a large variety of ionic liquids in order to improve the cellulose dissolution.^[5] The process is depending not only on the temperature but also on the cellulose (length of the polymer chains, crystallinity, impurities), on the amount of water in the cellulose itself and in the ionic liquids (highly hygroscopic). The most studied/efficient ionic liquids are composed of an imidazolium based cation with either a chloride or an acetate anion. Up to 25 wt% of cellulose have been dissolved in these ionic liquids at 100-120 °C. ^[5-6] This is comparable to the efficiency of the solvents used in industry with the advantage of allowing an easier recycling of the solvent because of the negligible vapor pressure of the ionic liquids. Chloride based ionic liquids tend to have a relatively high melting temperature which might limit their applications. For example, the melting point of the 1-butyl-3-methylimidazolium chloride ([Im₁₄]Cl) is 69 °C.^[7] Carboxylate based ionic liquids are liquid at lower temperatures but suffer stability issues and should be used below 120 °C while used for long process.^[8]

The search for new ionic liquids able to dissolve efficiently cellulose remains very active. An elucidation of the dissolution process could largely help in the selection of the best candidates. The role of the anion in the dissolution is now relatively well understood. It interacts through strong H-bonds with the hydroxyl groups of the cellulose. Using COSMO-RS (Conductor-like Screening Model for Real Solvents) Liu *et al.* have modeled the ability of hundreds of ionic liquids to dissolve cellulose.^[9] The calculated excess enthalpy was used to estimate how an ionic liquid interacts with the cellulose. These authors have concluded that the role of the cation is relatively small compared to the one of the anion. Molecular simulations studies have shown that while the anion takes place around the hydroxyl groups

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of the cellulose, the cation fits the apolar part of the cellulose in order to obtain the best interactions between solvent and cellulose.^[10] Lindman *et al.* observed that only amphiphilic solvents can dissolve cellulose meaning the hydrophobic interactions between the solvent and the cellulose are also necessary for the dissolution.^[11]

The addition of an aprotic and polar co-solvent like dimethylsulfoxide (DMSO), N,Ndimethylformamide (DMF) or N-methylpyrrolidinone (NMP) to an efficient ionic liquid improves the kinetics of cellulose dissolution.^[12] Nevertheless, the exact role of the co-solvent is still not perfectly understood. Interactions between mixtures of ILs (imidazolium acetate)/DMSO and cellulose or cellobiose were studied through the measurement of mixing/dissolution enthalpy using calorimetry.^[13] A slightly lower exothermicity was measured with the addition of DMSO as a co-solvent. This reduction of the enthalpy indicates less favorable interactions. Moreover, in a system cellulose + ionic liquid (imidazolium acetate) / DMSO (80/20 wt/wt), no direct molecular interaction between DMSO and cellulose was detected by molecular simulation.^[14] Ionic liquids are generally highly viscous and their viscosity can increase by up to 3 orders of magnitude in the presence of 10 to 15 wt% of cellulose in it.^[15] The addition of DMSO as a co-solvent to an already highly efficient ionic liquid (typically acetate anions) improves the dissolution by mainly decreasing the viscosity.^[16] The research for other co-solvents is still very active. Greener alternative like γ valerolactone are explored. ^[17] Biphasic mixtures composed of DMI (1,3-dimethyl-2imidazolidinone), ILs and cellulose are also studied to simplify the separation and recycling, as demonstrated in a recent work.^[18]

Ammonium-based ionic liquids have demonstrated their ability to dissolve cellulose with the advantage to be relatively cheap.^[19] Several groups have evaluated the efficiency of this family for cellulose dissolution with various results. Triethyloctylammonium chloride ($[N_{2228}]$ Cl) can dissolve up to 15 wt% of cellulose,^[20] diethyl-dimethylammonium acetate ($[N_{1122}][OAc]$) only 2 wt% at 100 °C,^[21] while in a third study several ionic liquids based on tetraalkylammonium (($[N_{1333}], [N_{1133}]$ and $[N_{1144}]$) acetate, levulinate and itaconate were able to dissolve up to 10 wt% of cellulose at 90–110 °C.^[17b] As for the imidazolium, the addition of a co-solvent to these ionic liquids increases the amount of cellulose dissolved up to 20 wt% at 90 °C.^[17b] The co-solvent is also useful for ionic liquids presenting high melting points. For example, in the case of tetrabutylammonium acetate ($[N_{4444}][OAc]$), which has a melting temperature around 100 °C, after the addition of a large amount of DMSO it has been found by Huang *et al.* that up to 8 wt% of cellulose could be dissolved.^[22] The effect of the presence of oxygenated functions in the alkyl chain of the ammonium was also considered. Ammonium

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based ionic liquids with ether groups like $[N_{122,102}]$ (N,N-diethyl-N-(2-methoxyethyl)-N-methylammonium) can dissolve cellulose up to 12 wt% at 100 °C,^[23] while in another study, it was found 18 wt% in $[N_{11,202,202}]$ [OAc] at 80 °C.^[24]

In the present work, our objective is to study the effect of the ions' size of ammonium based ionic liquids on their ability to dissolve cellulose. For that purpose, 20 ionic liquids containing a tetraalkylammonium cation and a carboxylate anion (acetate [OAc] and propionate [OPr]) have been synthesized. The cations considered are triethylalkylammonium ($[N_{222X}]$) and tripropylalkylammonium ($[N_{333X}]$) where X=4, 6, 8, 10 and 12 (butyl, hexyl, octyl, decyl and dodecyl). In this set of 20 ionic liquids, molecular interactions between the ions and the cellulose are not expected to change substantially and only size of the ions should explain the variation of cellulose, the 20 ionic liquids have also been studied with addition of a co-solvent (20 wt% DMSO / 80 wt% ionic liquid). In parallel to the dissolution experiments, viscosity of solvents and rheology of (cellulose + solvent) mixtures were measured with the aim to evaluate if transport properties could limit the dissolution. IR spectroscopy and molecular simulation were used to evaluate the molecular interactions of these systems.

Results and Discussion

The temperature generally used in studies for cellulose dissolution in ionic liquid is between 80 to 120 °C.^[5] However, we have noticed that ammonium carboxylate based ionic liquids are not stable at high temperatures. During cellulose dissolution in [N₂₂₂₆][OAc] at 100 °C a strong coloration of the sample was observed within few hours which was not observed at 80°C. To explore thermal stability of this ionic liquid, pure [N₂₂₂₆][OAc] was heated at 100°C for 24 hours under inert atmosphere and the sample was then analyzed by ¹H NMR and IR spectroscopies. NMR analysis shows that 20–30% of ethyl and hexyl acetates (IR: v= 1730 cm⁻¹) are produced in a ratio 3/1 respectively accompanied by the same amount of triethylamine. This is explained by the random displacement of the alkyl groups by the nucleophilic acetate at high temperature. At 80°C, the same experiment leads to only traces amount of decomposition (less than 1% after 24h and approximately 2% after 48h). Thus, our study will mainly focus on dissolution of cellulose at 80 °C or lower.

Temperature of dissolution



Figure 1: Comparison of the temperature of dissolution of 10 wt% of microcrystalline cellulose in pure $[N_{222X}][OAc]$ (top) and in mixtures of $[N_{222X}][OAc]/DMSO$ (80/20 wt%) (bottom).

The impact of the ion's size is first studied by comparing the temperature of dissolution of 10 wt% of cellulose in the 20 ionic liquids. The evolutions of the brightness obtained for the 5 triethyl-alkyl-ammonium acetate ($[N_{222X}][OAc]$, X=4, 6, 8, 10 and 12) are given in Figure 1. In the case of $[N_{2224}][OAc]$, the brightness is increasing during the experiment and cellulose is not dissolved. The experiment was repeated with only 1 wt% of cellulose and even in that case no dissolution could be observed. For the other 4 ionic liquids, all the cellulose is dissolved at temperatures between 70 and 90 °C.

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The impact of the addition of a co-solvent can also be observed in Figure 1. Even with the addition of 20 wt% of DMSO as co-solvent, $[N_{2224}]$ [OAc] is still not able to dissolve any cellulose. For the other 4 ionic liquids, the addition of DMSO helps to decrease the temperature of dissolution (between 50 and 60°C instead of 70 – 90 °C without DMSO). In fact, in all these cases the dissolution starts as soon as the experiment. In the case of the two longer chains (X=10 and 12), it exists a shoulder (10% in intensity of the maximal brightness) which is an indication that the last fragments of cellulose are more difficult to dissolve (origin of the shoulder will be discussed in more details in the rheology section). To compare all 20 ionic liquids, with and without co-solvent, T_{onset} and $T_{10\%}$ (°C) are given in Table 1. T_{onset} corresponds to the beginning of an event) while the $T_{10\%}$ corresponds to the end to the dissolution (as used in DSC (differential scanning calorimetry to define the beginning of an event) while the $T_{10\%}$ corresponds to the end to the dissolution of 10 wt% of cellulose (temperature of the first image without any particle).

Table 1: Temperature (°C) of dissolution of 10 wt% of microcrystalline cellulose with a heating ramp of 0.25° C/min up to 90 °C. T_{onset} and T_{10%} correspond to the beginning and the end of the dissolution, respectively. Solvents with DMSO are composed of 80/20 (wt/wt) of ionic liquid and DMSO. (-) no cellulose dissolution observed, (*) dissolution begins as soon as experiment is started.

T (°C)		[N _{222X}]	[N _{222X}]	[N _{333X}]	[N _{333X}]
I onse	et (C)	[OAc]	[OPr]	[OAc]	[OPr]
	X=4	-	-	-	-
П	X=6	51	60*	80	-
lre	X=8	51	60*	74	77
Pl	X=10	57	70*	77	85
	X=12	68*	67*	-	-
0	X=4	-	-	-	-
MS	X=6	35*	34*	43	-
D	X=8	35*	32*	38*	66
/ith	X=10	34*	31*	36*	67
5	X=12	31*	32*	36*	68
т	(° C)	[N _{222X}]	[N _{222X}]	[N _{333X}]	[N _{333X}]
T _{10%}	_ω (°C)	[N _{222X}] [OAc]	[N _{222X}] [OPr]	[N _{333X}] [OAc]	[N _{333X}] [OPr]
T _{10%}	^{√₀} (°C) X=4	[N _{222X}] [OAc]	[N _{222X}] [OPr]	[N _{333X}] [OAc]	[N _{333X}] [OPr]
T _{10%}	√₀ (°C) X=4 X=6	[N _{222x}] [OAc] - 73	[N _{222X}] [OPr] - 79*	[N _{333X}] [OAc] - -	[N _{333X}] [OPr] - -
	x=4 X=6 X=8	[N _{222X}] [OAc] - 73 79	[N _{222X}] [OPr] - 79* 77*	[N _{333X}] [OAc] - -	[N _{333X}] [OPr] - -
Dure IL	x=4 X=6 X=8 X=10	[N _{222X}] [OAc] - 73 79 80	[N _{222X}] [OPr] - 79* 77* 90*	[N _{333X}] [OAc] - - -	[N _{333X}] [OPr] - - -
Dure IL	x=4 X=6 X=8 X=10 X=12	[N _{222X}] [OAc] - 73 79 80 89*	[N _{222X}] [OPr] - 79* 77* 90* 89*	[N _{333X}] [OAc] - - - - -	[N _{333X}] [OPr] - - - - -
T _{10%}	x=4 X=6 X=8 X=10 X=12 X=4	[N _{222X}] [OAc] - 73 79 80 89* -	[N _{222X}] [OPr] - 79* 77* 90* 89*	[N _{333X}] [OAc] - - - - - - -	[N _{333X}] [OPr] - - - - - - -
MSO Pure IL	x=4 X=6 X=8 X=10 X=12 X=4 X=6	[N _{222X}] [OAc] - 73 79 80 89* - 46*	[N _{222X}] [OPr] - 79* 77* 90* 89* - 62*	[N _{333X}] [OAc] - - - - - - - 90	[N _{333X}] [OPr] - - - - - - - - -
DMSO Pure IL	X=4 X=6 X=8 X=10 X=12 X=4 X=6 X=8	[N _{222X}] [OAc] - 73 79 80 89* - 46* 52*	[N _{222X}] [OPr] - 79* 77* 90* 89* - 62* 48*	[N _{333X}] [OAc] - - - - - 90 62*	[N _{333X}] [OPr] - - - - - - - 84
Vith DMSO Pure IL	X=4 X=6 X=8 X=10 X=12 X=4 X=6 X=8 X=10	[N _{222X}] [OAc] - 73 79 80 89* - 46* 52* 55*	[N _{222X}] [OPr] - 79* 77* 90* 89* - 62* 48* 62*	[N _{333X}] [OAc] - - - - - - 90 62* 69*	[N _{333X}] [OPr] - - - - - - - 84 78

The analysis of the dissolution temperatures on the 20 ionic liquids leads to the following remarks:

- With or without co-solvent, ionic liquids with the short butyl chain ($[N_{2224}][OAc]$, $[N_{2224}][OPr]$, $[N_{3334}][OAc]$ and $[N_{3334}][OPr]$) are not able to dissolve cellulose. Even with only 1 wt% of cellulose, no dissolution was observed.

- Without co-solvent, the temperatures obtained for $[N_{222X}]$ are lower than for $[N_{333X}]$ cation. Moreover, temperature of dissolution in $[N_{222X}]$ [OAc] are lower than in $[N_{222X}]$ [OPr].

- For all ionic liquids efficient for the cellulose dissolution, as already observed with Figure 1 in the case of $[N_{222x}][OAc]$, the addition of co-solvent decreases the temperature of

dissolution by more than 10 °C, in average around 20 °C. After addition of co-solvent, most ionic liquids are starting to dissolve cellulose below 40 °C. For 6 ionic liquids, the presence of DMSO allows the dissolution of 10 wt% of cellulose that was impossible in the pure ionic liquid (case of $[N_{333X}][OAc]$ with X=6, 8, 10 and 12 of $[N_{333X}][OPr]$ with X=8 and 10).





Figure 2: Evolution of the brightness during dissolution of several amounts of microcrystalline cellulose in $[N_{2228}][OAc]$ with and without co-solvent (80/20 wt%) with a heating ramp of 0.25°C/min.

Dissolution of different quantities of cellulose has been realized in order to estimate the maximal amount that can be dissolved in each ionic liquid. As example, few dissolution experiments realized on $[N_{2228}][OAc]$ with and without co-solvent are given in Figure 2. Without DMSO, the dissolution process occurs mainly between 50 and 70 °C. 10 wt% of

cellulose is fully dissolved at 80 °C while 15 wt% is almost completely dissolved at 90 °C. The brightness is stable and still over 50 with 19 wt% of cellulose at the end of the experiment (90° C).

With DMSO the cellulose dissolves 20 °C below the pure ionic liquids. Up to 20 wt% of cellulose can be dissolved before reaching 70 °C, but the brightness stays high for 22 and 25 wt% of cellulose. The large difference of brightness for only few percent of undissolved cellulose illustrates the sensitivity of this technique to detect the last particles of cellulose. The maximal amount of cellulose that can be dissolved at 80 °C is then 12 wt% in pure $[N_{2228}][OAc]$ (another experiment was done with this amount of cellulose but is not shown in Figure 2 for clarity reason) and 20 wt% in $[N_{2228}][OAc]/DMSO$.

With this procedure, the amount of dissolved cellulose can be underestimated up to 2 wt% because not all the cellulose quantities were tested. After the analysis of the 20 ionic liquids with this protocol, it appears that the highest amount of cellulose dissolved is 15 wt% at 80 °C and 22 wt% at 90 °C in [N₂₂₂₆][OAc]. The results at 80 °C (heating rate of 0.25 °C/min) for all ionic liquids with and without co-solvent are given in Figure 3.



Figure 3: Maximal amount of microcrystalline cellulose dissolved at 80 °C with a heating rate of 0.25 °C/min for 20 ionic liquids without and with 20 wt% of DMSO as co-solvent.

 $[N_{2224}][OAc], [N_{2224}][OPr], [N_{3334}][OAc] and [N_{3334}][OPr])$ cannot dissolve any cellulose. Without co-solvent, 5 ionic liquids are capable to dissolve at least 10 wt% of cellulose at 80 °C ($[N_{2226}][OAc], [N_{2228}][OAc], [N_{22210}][OAc], [N_{2226}][OPr]$ and $[N_{2228}][OPr]$). Without co-solvent, none of the $[N_{333X}]^+$ based ionic liquids are capable of dissolving any cellulose. The addition of co-solvent increases the amount of cellulose dissolved, up to 20 wt% in $[N_{2226}][OAc]/DMSO$ and $[N_{2228}][OAc]/DMSO$ and 12 ionic liquids are capable of dissolving at least 10 wt% of cellulose. A correlation exists between the amount of cellulose dissolved at 80 °C in pure ionic liquids and the temperature of dissolution; the ionic liquids capable to dissolve at the lowest temperatures are also those dissolving the most.

Number of anion per glucose unit

The weight of cellulose dissolved per weight of solvent is not necessarily the most accurate method to compare the efficiency of ions. The strongest interactions between the ionic liquids and cellulose are H-bonds between the anions and the hydroxyl groups of the cellulose. The ability of an ionic liquid to dissolve cellulose can be expressed by the APG ratio (moles of Anions Per moles of Glucose units) at the highest amount of cellulose dissolved in each ionic liquid. Lower is this ratio, better is the solvent. Every acetate anion can be acceptor of 2 H-bonds while every glucose unit of the cellulose can be donor of 3 H-bonds with 3 hydroxyl groups (with the exception of the end groups of the polymer chain). Thus, in theory, the lowest APG ratio would be 1.5 (obtained when all anions interact with every hydroxyl group of the cellulose). The APG ratio values obtained in the present work are given in Table 2.

Table 2: Number of anions per glucose unit (APG ratio) calculated from the dissolution experiments presented in Figure 3. (-) less than 1 wt% of microcrystalline cellulose could be dissolved. The number is in red when the ionic liquid is giving a better result than the reference ionic liquid $[Im_{12}][OAc]$.

		[N _{222X}]	[N _{222X}]	[N _{333X}]	[N _{333X}]
		[OAc]	[OPr]	[OAc]	[OPr]
Г	X=4	-	-	-	-
	X=6	4.2	6.3	-	-
Ire]	X=8	4.8	5.6	-	-
Pu	X=10	5.4	-	-	-
	X=12	-	-	-	-
0	X=4	-	-	-	-
4SC	X=6	2.4	2.7	9.5	-
DI	X=8	2.1	2.3	2.6	5.0
ith	X=10	2.2	2.1	2.4	2.3
'n	X=12	2.7	3.8	3.5	4.3

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The APG ratio obtained without co-solvent for the ammonium based ionic liquids are between 4.2 and 6.3. As comparison, the ability of a benchmark ionic liquid (1-ethyl-3methylimidazolium chloride acetate, $[Im_{12}][OAc]$) has been evaluated for cellulose dissolution with the same procedure. A value of 5.1 anion/glucose unit (corresponding to 17 wt% of cellulose) was obtained in this pure ionic liquid. Two of the ammonium based ionic liquids ($[N_{2226}][OAc]$ and $[N_{2228}][OAc]$) are thus more efficient than $[Im_{12}][OAc]$. These two ionic liquids are the two based on $[N_{222X}]$ which are liquids at room temperature. This may indicate that the reason why imidazolium are good cations for cellulose dissolution is not related only to the aromaticity or to the acidic proton of the imidazolium ring as proposed in literature.^[25]

The dissolution of cellulose in $[Im_{12}][OAc]$ with the addition of 20 wt% of DMSO was also measured in the present work. The addition of co-solvent is almost not changing the mass of cellulose dissolved (18 wt%) per mass of solvent (ionic liquid + DMSO). Thus it induces a decrease by around 20% of APG (equal to 3.9 in [Im₁₂][OAc]/DMSO). In presence of DMSO, 12 ammonium based ionic liquids are capable of dissolving higher amounts of cellulose compared to the $[Im_{12}][OAc] + DMSO$ (in red in Table 2). This approach confirms roughly the results observed when working with the mass of dissolved cellulose (Figure 3). However, by using the APG ratio, a more precise description of the impact of alkyls' sizes can be [N₃₃₃₁₀][OPr]/DMSO obtained. For example, seems much less efficient than [N₂₂₂₆][OAc]/DMSO when using the wt% (15 vs 20 wt%). In fact the cellulose dissolution is similar in both ionic liquids when looking at the APG ratio meaning at molecular level, the number of ions interacting with cellulose is the same in both ionic liquids.

In summary, two ionic liquids ($[N_{2226}][OAc]$ and $[N_{2228}][OAc]$) are capable to dissolve high amounts of cellulose even without co-solvent at 80 °C. The addition of DMSO decreases the dissolution temperature, allowing 12 ionic liquids to dissolve more cellulose than the benchmark imidazolium based ionic liquid. Among these, the 10 most efficient are all dissolving similar amounts of cellulose (corresponding to 2.5 APG). Ionic liquids with $[N_{YYY6}]$, $[N_{YYY8}]$ and $[N_{YY10}]$ cations are the most efficient for cellulose dissolution. The longest $[N_{YY12}]$ are not as effective while the shortest $[N_{YY4}]$ cannot dissolve any cellulose.

In the second part of this article, several properties of these ionic liquids will be measured and correlated with their ability to dissolve cellulose. The main objective is to identify which properties are 1) controlled by the size of the ions and 2) impacting their ability to dissolve cellulose.

Viscosity

The presence of 20 wt% of DMSO tends to improve the ability to dissolve cellulose (dissolution at lower temperatures and higher amounts of cellulose dissolved). One of the main effects of the addition of a co-solvent in an ionic liquid is to decrease considerably its viscosity. The viscosities of pure ammonium based ionic liquids have been measured as a function of temperature and are given in the Figure 4. The viscosity of only 9 of the 20 ionic liquids could be measured for practical reasons. As the quantity of water in the samples is typically 0.5 wt%, we estimate that the measured viscosity is lower, by at least 20%, than the viscosity of the dried ionic liquids.^[26] The fluctuations in the amount of water between ionic liquids should induce errors of around 10 to 20% in between two ionic liquids. Even though, comparisons and conclusions can be established.



Figure 4: Viscosity of 9 ammonium carboxylate based ionic liquids (with around 5000 ppm of water). Symbols: circles for acetate, squares for propionate based ionic liquids, full symbols for $[N_{222X}]$ and empty symbols for $[N_{333X}]$ cations. For the length of the longer alkyl chain of the cation: red = hexyl, green = octyl, blue = decyl and black = dodecyl.

The less viscous ionic liquid is $[N_{2226}][OAc]$ with a viscosity of 1200 mPa.s at 25 °C, much higher than the one of imidazolium based ionic liquids: 139 mPa.s for $[Im_{12}][OAc]^{[27]}$ and 441 mPa.s for $[Im_{14}][OAc]^{[28]}$ at the same temperature. The 3 ionic liquids with the lowest viscosities are $[N_{2226}][OAc]$ (88 mPa.s at 60°C), $[N_{2226}][OPr]$ (102 mPa.s at 60°C) and $[N_{2228}][OPr]$ (121 mPa.s at 60°C). The other 6 ionic liquids, with longer alkyl chains, have much higher viscosities (between 178 and 250 mPa.s at the same temperature). This increase

of the viscosity with the alkyl chain length was already observed on other ammonium ionic liquids.^[29]

The more viscous ionic liquids are also those not dissolving cellulose without co-solvent indicating viscosity is probably a limiting parameter. The addition of 20 wt% of DMSO decreases by around 80% the viscosity. In presence of DMSO all ionic liquids are largely less viscous than any pure; the maximum viscosity is 31 mPa.s at 60 °C after addition of DMSO (for $[N_{3334}][OAc]/DMSO$) while the minimum viscosity of a pure ionic liquid is 88 mPa.s at 60°C. If viscosity would be the only parameter that explains fluctuation of the ability to dissolve cellulose within similar ionic liquids, this would mean that after addition of DMSO, all ionic liquids should have similar efficiency. This was observed for most ionic liquids (with an APG ratio around 2.5 as can be seen in Table 2) but not in all cases. For example, $[N_{YY12}]$ has the tendency to be less efficient and $[N_{YY4}]$ based ionic liquid cannot dissolve any cellulose. The fact that some ionic liquids are less effective ($[N_{YY12}]$) or unable ($[N_{YY4}]$) to dissolve cellulose in presence of DMSO cannot be explained by their viscosity.

Rheology



Figure 5: Complex viscosity modulus (η^*) of systems composed of 10 wt% of microcrystalline cellulose in [N₂₂₂₆][OAc]/DMSO (a) and [N₃₃₃₁₂][OAc]/DMSO (b) after dissolution. (c) Evolution of the brightness of a sample containing 10 wt% of microcrystalline cellulose in [N₂₂₂₆][OAc]/DMSO and [N₃₃₃₁₂][OAc]/DMSO as function of the temperature with a heating rate of 0.25 °C/min.

To explore in more details the effect of transport limitations, rheological measurements at different temperatures have been done on $[N_{2226}][OAc]/DMSO$ and $[N_{33312}][OAc]/DMSO$ containing 10 wt% of pre-dissolved cellulose. $[N_{2226}][OAc]/DMSO$ is one of the efficient solvent (APG ratio = 2.4) while $[N_{33312}][OAc]/DMSO$ is one of the poorly efficient solvent

(APG ratio = 3.5). This later can dissolve cellulose but not as much as other tetralkylammonium based ionic liquids. The evolution of the brightness during the dissolution of 10 wt% of cellulose in these two ionic liquids using optical microscopy is presented in Figure 5c. In Figure 5 (a and b), the moduli of the complex viscosity η^* is plotted versus the frequency for both ionic liquids at different temperatures. In the case of [N₂₂₂₆][OAc]/DMSO (7a) a unique viscoelastic behavior can be observed with viscosities ranging from about 1 to 100 Pa.s. [N₃₃₃₁₂][OAc]/DMSO presents a different viscoelastic behavior (7b). For temperatures higher than 70 °C the same behavior as previously can be observed, but, for temperatures lower than 70 °C a sharp transition in the viscoelastic behavior to a gel-solid like behavior. At the lowest temperature the material behaves like a gel with an infinite viscosity at zero frequency and even the addition of a co-solvent as DMSO does not allow preventing the formation of a gel.

From Figure 5 (c), it can be seen that the two ionic liquids behave differently in brightness analysis. In the case of $[N_{33312}]$, a shoulder appears in the brightness curve between 40 and 70°C (similarly to what was observed in Figure 1). This result is consistent with the formation of a gel observed during the rheology experiments. The viscosity of the solution is very high leading to great diffusion times. It has already been reported that imidazolium acetate based ionic liquids also induce a gel phase when more than 12 wt% of cellulose is dissolved.^[30] When a gel is generated during the dissolution, the time needed to complete the dissolution will be dramatically increased and therefore ionic liquids that avoid gelation should be preferred.

<u>Spectroscopy</u>

When diffusion is not the limiting parameter in the dissolution process, as in the case of $[N_{XXX4}]$ based ionic liquids, a careful study of the interactions (between anions, cations and cellulose) can be helpful to understand the solvents efficiency in cellulose dissolution.



Figure 6: Part of the infrared spectra of $[N_{2224}][OAc]$ and $[N_{2226}][OAc]$. Spectra have been shifted for clarity.

A strong interaction between the anion and cation might explain why some ionic liquids ([N_{XXX4}] in the present case) cannot dissolve cellulose. A competition to create H-bond with the acetate anion might exist between cation and cellulose and a stronger interaction between anion and cation could decrease the ability of the ionic liquid to interact with the cellulose and to dissolve it. The strength of the interactions between anions and cations can be observed by IR spectroscopy. Figure 6 presents the IR spectra of [N₂₂₂₄][OAc] and [N₂₂₂₆][OAc], respectively a non-efficient and the most efficient ionic liquid. In dried ionic liquids (0.5 wt% H₂O), the positions of the COO⁻ asymmetric (v_{as} at 1580 cm⁻¹) and symmetric (v_s at 1365 cm⁻¹ ¹) stretching modes are not depending on the cation. These two bands are an efficient probe of the strength of the interactions with the carboxyl group. Only the symmetric stretching mode is shifted by 1 cm⁻¹. As the comparison, with imidazolium cation ($[Im_{14}][OAc]$), these two modes are shifted by 20 cm⁻¹ at 1560 and 1384 cm⁻¹.^[31] Imidazolium cations are interacting stronger than ammonium with their acid proton of the aromatic ring. The specific interaction of the imidazolium ring does not appear necessary to improve the properties of the solvent. In fact, the absence of H-bond donor in ammonium cation could benefit to the interaction between anion and cellulose since the anion is only able to make H-bonds with the hydroxyl groups of the cellulose.

Similarly, when water is absorbed in the ammonium based ionic liquids, water molecules are interacting via H-bonds with the acetate and both bands are also shifted; as example, in $[N_{2226}][OAc]$ with 5–10 wt% of water (enough for water molecules to interact with every

anion), the two COO⁻ stretching modes are at 1573 and 1383 cm⁻¹. It appears then clearly that both ammonium cations interact similarly and weakly with the carboxylate anion. The strength of the interaction between ions cannot explain why ionic liquids with the smaller cations cannot dissolve cellulose.

Molecular structure

Table 3: Percentage of hydroxyl groups of a cellohexaose (Cell.) involved as donor in a hydrogen bond in 4 solvents: $[N_{2224}][OAc]$, $[N_{2226}][OAc]$ with and without DMSO calculated by molecular simulation.

Donor		Cell.	
Acceptor	Anion	Cell.	DMSO
[N ₂₂₂₄]	74 %	6 %	-
[N ₂₂₂₆]	70 %	6 %	-
[N ₂₂₂₄]/DMSO	74 %	7 %	0.2 %
[N ₂₂₂₆]/DMSO	70 %	7 %	0.4 %

The interactions between ions and cellulose were studied by molecular simulation with the aim to clarify why the smaller [N₂₂₂₄] cannot dissolve cellulose as efficiently as [N₂₂₂₆] cation. A cellulose oligomer (cellohexaose) has been simulated in 4 solvents $[N_{2224}][OAc]$ and [N₂₂₂₆][OAc] with and without DMSO. The structure of the solvents around the oligomer has been carefully studied in particular with radial distribution functions. No observable difference between the structures of the solvents could explain why ionic liquids with the smaller $[N_{2224}]$ cation could be a worse solvent. The most important interaction between the ions and cellulose is the H-bonds between the anion and the hydroxyl groups of the cellulose.^[32] The probabilities of the hydroxyls groups of the oligomer to form H-bonds with the solvents are given in Table 3. Each hydroxyl group of the cellulose oligomer is donor of an H-bond most of the time; between 76 and 81%. Generally the acceptor of the H-bond is the acetate anion (70–74%), sometime the H-bond is intramolecular (6–7%) and the co-solvent is almost never directly involved with the oligomer (0.2–0.4%). The number of H-bonds is even higher in the case of [N₂₂₂₄][OAc] than for [N₂₂₂₆][OAc] indicating than [N₂₂₂₄][OAc] should be a very efficient solvent for cellulosic polymer chains. With their molecular simulation study Cho et al. explained that the cation interacts also with the cellulose and mainly via the side chain and the linker oxygens between the glucose cycles.^[32] Structure and interactions

10.1002/cssc.201601830

between the cation and the oligomer was scrutinized and no difference could be observed between the two ionic liquids. These results from molecular simulation shows that energetically $[N_{2224}][OAc]$ seems a better solvent for an oligomer of cellulose than $[N_{2226}][OAc]$.

Discussion

Size of the ions can have a dramatic impact on the ability of an ionic liquid to dissolve cellulose. Ionic liquids studied in this work can be ranked in 4 groups:

- efficient ionic liquids, capable to dissolve at least 10 wt% of cellulose even without cosolvent: only based on $[N_{222X}]$ cations with X=6, 8 or 10. $[N_{2226}][OAc]$ is dissolving up to 15 wt% of cellulose at 80 °C (22 wt% at 90 °C and 20 wt% in presence of DMSO at 80 °C). The ability to dissolve cellulose in these ammonium based ionic liquid is comparable to this of the benchmark imidazolium based ionic liquid ($[Im_{12}][OAc]$).

- efficient ionic liquids only after addition of co-solvent. While in pure ionic liquids, only the less viscous ionic liquids are capable to dissolve cellulose at 80 °C or below, after addition of DMSO, 10 ionic liquids are dissolving similar amount of cellulose: around 2.5 anions per glucose unit. The addition of 20 wt% of DMSO decreases enough the viscosity to overcome this limitation of some ionic liquids.

- poorly efficient ionic liquids which tend to dissolve less cellulose even with 20 wt% of DMSO. These ionic liquids form a gel when dissolving cellulose even in presence of co-solvent. The temperature should then be increased to suppress the gel structure and continue the dissolution. This effect has particularly been observed with ionic liquids having the longest alkyl chains: $[N_{YY12}]$.

- inefficient ionic liquids are generally based on the smallest $[N_{YYY4}]$ cations. These ionic liquids are not able to dissolve any cellulose at temperature below 80 °C. The viscosity or gelation cannot explain this impossibility to dissolve cellulose since even small amounts of cellulose in presence of co-solvent cannot be dissolved. As shown by infrared spectroscopy, the interactions between anion and cation are similar in $[N_{2224}][OAc]$ and in $[N_{2226}][OAc]$. Moreover, molecular simulation illustrated that the direct molecular interactions responsible of cellulose dissolution (namely H-bonds), are equivalent between cellulose oligomer and the ions of $[N_{2224}][OAc]$ or $[N_{2226}][OAc]$. Dissolution of crystalline cellulose is a complex phenomenon and a cooperative interaction between many ions and cellulose has to exist in order to start the cellulose dissolution.

Conclusions

The ability to dissolve cellulose at 80 °C has been established for 20 tetraalkylammonium carboxylate. The ionic liquids could be classified in 4 groups from highly efficient to inefficient cellulose solvents demonstrating the effect of the size of the ions on the dissolution ability. Viscosity, rheology, spectroscopy and molecular simulation were used to correlate the ionic liquid's properties with their ability to dissolve cellulose. The inefficiency of the smallest cations tested could also be due to an insufficient interaction with the hydrophobic parts of the cellulose. Complementary studies will be necessary to test how the amphiphilic structures of the cellulose and the ionic liquid associate with efficient and inefficient ionic liquids (e.g. with [N₂₂₂₆][OAc] and [N₂₂₂₄][OAc]). In particular, more advanced molecular simulations with cellulose microfibrils^[10] could describe the molecular organization at the interface between the liquid and the undissolved polymer.

Experimental Section

Materials

Avicel PH101 with particle size of 50 μ m was supplied by Sigma and dried at 100 °C for 24 hours before use. DMSO (puriss, > 99.9%), tripropylamine (>98%), 1-bromobutane (>98%), 1-bromooctane (>98%) and 1-bromodecane (>98%) were obtained from Fluka. Triethylamine (99%) was obtained from Acros while acetic (>99%) and propionic (99%) acids were purchased from VWR and Merck, respectively. [Im₁₂][OAc] was obtained from Iolitec (>98%). Syntheses were carried in parallel (10) using a caroussel reaction station (Radleys). pH was recorded on a Metler Toledo, seven compact.

Synthesis

Tetraalkylammonium bromide. In each reaction tube of the caroussel station were introduced 10 mL of acetonitrile, 44.6 mmol of triethyl or tributyl amine and 37.1 mmol of the desired bromoalcane. The temperature is increased to 85°C and the reaction mixture is stirred 24–48^h. The reaction mixture is purred in 150 mL of water and extracted with ether (2X50mL). Evaporation of the aqueous phase affords a viscous oil which is left under reduced pressure (1 mbar) for 48h to afford a white solid.

Tetraalkylammonium acetate and propionate. The tetraalkylammonium bromide were dissolved in 150 mL of water and passed through a Dowex® 1X2 (50 grammes) column charged with hydroxide ions followed by washing with 250 mL of water. The volume was reduced to 150 mL under reduced pressure. The column was recharged with NaOH, then

washed with water under pH reach 7, and the exchange of anion of tetraalkylammonium was repeated. This process was performed at least 3 times. The final aqueous solution was concentrated under reduced pressure to 150–200 mL, then neutralized to pH=5.2 (pHmeter) with the appropriate carboxylic acid. Evaporation under vacuum of the solution furnished a colorless liquid. Evaporation under vacuum (0.1 mbar) for at least 48h yields the desired ionic liquid as a pale yellow product. Water content (measured by KF titration) in ionic liquid was systematically lower than 1 wt% and generally around 5.000 ppm and only 10 ionic liquids remain liquid at room temperature (Table 4) but all are liquid at 60°C.

Table 4: Phase of tetraalkylammonium carboxylate ionic liquids at room temperature.

S=Solid, L=Liquid.				
	[N _{222X}]	[N _{222X}]	[N _{333X}]	[N _{333X}]
	[OAc]	[OPr]	[OAc]	[OPr]
X=4	S	S	S	S
X=6	L	S	L	L
X=8	L	S	L	L
X=10	S	S	L	L
X=12	S	S	L	L

Triethyl butyl ammonium acetate, $[N_{2224}][OAc]$:RMN-¹H (400 MHz, D₂O): δ (ppm) = 3.19 (q, *J*=7.3Hz, 6H), 3.08 (m, 2H), 1.83 (s, 3H),1.57 (m, 2H), 1.30 (hex, *J* = 7.3Hz, 2H), 1.18 (3xt, *J* = 7.3 Hz, 9H), 0.88 (t, *J* = 7.3Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 172.0, 55.6, 51.8, 26.3, 22.9, 19.9, 13.5, 7.2. IR v (neat, cm⁻¹): 2982, 1584, 1483, 1462, 1368, 1180, 1028, 800.

Triethyl butyl ammonium proprionate, $[N_{2224}][OPr]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.20 (q, *J*=7.3Hz, 6H), 3.08 (m, 2H), 2.10 (q, *J*=7.7Hz, 2H), 1.58 (m, 2H), 1.31 (hex, *J* = 7.5Hz, 2H), 1.19 (3xt, *J* = 7.3 Hz, 9H), 0.98 (t, *J* = 7.7Hz, 3H), 0.88 (t, *J* = 7.3Hz). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 175.0, 55.7, 52.0, 31.9, 22.9, 19.2, 13.7, 11.7, 7.1. IR v (neat, cm⁻¹): 2963, 1572, 1392, 1095, 901, 799.

Triethyl hexyl ammonium acetate, $[N_{2226}][OAc]$:RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.16 (q, *J*=7.3Hz, 6H), 3.03 (m, 2H), 1.79 (s, 3H),1.55 (m, 2H), 1.23 (m, 6H), 1.15 (3xt, *J* = 7.3 Hz, 9H), 0.78 (t, *J* = 7.3Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆) : δ (ppm) = 172.0, 56.0, 51.9, 30.6, 26.3, 25.5, 21.9, 20.9, 13.7, 7.2. IR v (neat, cm⁻¹) : 2963, 1584, 1370, 1165, 997, 893, 802.

Triethyl hexyl ammonium propionate, $[N_{2226}][OPr]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.18 (q, *J*=7.3Hz, 6H), 3.06 (m, 2H), 2.09 (q, *J*=7.7Hz, 2H),1.58 (m, 2H), 1.26 (m, 6H), 1.17 (3xt, *J* = 7.3 Hz, 9H), 0.97 (t, *J* = 7.7Hz, 3H), 0.79 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆) : δ (ppm) = 175.4, 56.0, 51.9, 31.8, 30.6, 25.5, 21.9, 20.9, 13.7, 11.6, 7.2. IR v (neat, cm⁻¹): 2963, 1578, 1460, 1377, 1354, 851, 812.

Triethyl octyl ammonium acetate, $[N_{2228}][OAc]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.19 (q, *J*=7.3Hz, 6H), 3.06 (m, 2H), 1.83 (s, 3H),1.58 (m, 2H), 1.28 (m, 10H), 1.18 (3xt, *J* = 7.3 Hz, 9H), 0.80 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 172.0, 56.0, 51.9, 31.1, 28.5, 28.4, 26.3, 25.9, 22.0, 21.0, 13.9, 7.2. IR v (neat, cm⁻¹): 2928, 1584, 1458, 1371, 1161, 1005, 893, 800.

Triethyl octyl ammonium propionate, $[N_{2228}][OPr]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.20 (q, *J*=7.3Hz, 6H), 3.07 (m, 2H), 2.10 (q, *J*=7.7Hz, 2H), 1.59 (m, 2H), 1.29 (m, 10H), 1.19 (3xt, *J* = 7.3 Hz, 9H), 0.98 (t, *J* = 7.7Hz, 3H), 0.80 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆) : δ (ppm) = 175.1, 56.0, 51.9, 31.8, 31.2, 28.5, 28.4, 25.8, 22.0, 21.0, 13.9, 11.6, 7.2. IR v (neat, cm⁻¹): 2926, 1576, 1458, 1379, 1354, 1282, 1176

Triethyl decyl ammonium acetate, $[N_{22210}][OAc]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.21, 3.05 (m, 2H), 1.83 (s, 3H), 1.58 (m, 2H), 1.29 (m, 14H), 1.20 (m, 9H), 0.83 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆) : δ (ppm) = 172.0, 56.0, 51.9, 31.2, 28.9, 28.8, 28.7, 28.5, 26.1, 25.8, 22.0, 21.0, 13.8, 7.2. IR v (neat, cm⁻¹): 2926, 1583, 1458, 1371, 1161, 1010, 893, 800

Triethyl decyl ammonium propionate, $[N_{22210}][OPr]$: RMN-¹H (400 MHz, D₂O): δ (ppm) = 3.21 (q, *J*=7.3Hz, 6H), 3.07 (m, 2H), 2.11 (q, *J*=7.7Hz, 2H), 1.59 (m, 2H), 1.30 (m, 14H), 1.20 (3xt, *J* = 7.3 Hz, 9H), 0.99 (t, *J* = 7.7Hz, 3H), 0.82 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 175.1, 56.0, 51.9, 31.8, 31.3, 28.9, 28.8, 28.7, 28.5, 25.9, 22.1, 21.0, 13.8, 11.6, 7.2. IR v (neat, cm⁻¹): 2926, 1580, 1458, 1379, 1352, 1280, 1190, 1161, 1013, 854, 808

Triethyl dodecyl ammonium acetate, $[N_{22212}][OAc]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.17 (q, *J*=7.3Hz, 6H), 3.02 (m, 2H), 1.80 (s, 3H),1.54 (m, 2H), 1.25 (m, 18H), 1.16 (m, 9H), 0.78 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆) : δ (ppm) = 172.0, 56.0, 51.9, 31.3, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 26.2, 25.8, 22.1, 21.0, 13.9, 7.2. IR v (neat, cm⁻¹): 2918, 1585, 1470, 1381, 1030, 1008, 900, 795.

Triethyl dodecyl ammonium propionate, $[N_{22212}]$ [**OPr**] : RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.17 (q, *J*=7.3Hz, 6H), 3.01 (m, 2H), 2.05 (q, *J*=7.7Hz, 2H),1.54 (m, 2H), 1.25 (m, 18H), 1.16 (m, *J* = 7.3 Hz, 9H), 0.94 (t, *J* = 7.7Hz, 3H), 0.79 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆) : δ (ppm) = 175.1, 56.0, 51.9, 31.8, 31.3, 29.1, 29.0, 28.9, 28.8, 28.7, 28.5, 25.9, 22.1, 21.0, 13.9, 11.6, 7.2. IR v (neat, cm⁻¹): 2926, 1580, 1458, 1379, 1352, 1280, 850, 806.

Tripropyl butyl ammonium acetate, $[N_{3334}][OAc]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 2.77 (m, 8H), 1.52 (s, 3H), 1.30 (m, 8H), 0.97 (hex, J = 7.3Hz, 2H), 0.56 (t, J = 7.3Hz, 12H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 172.0, 59.2, 57.6, 26.3, 23.1, 19.2, 14.8, 13.4, 10.5. IR v (neat, cm⁻¹): 2967, 2941, 2915, 2876, 1586, 1474, 1368, 1316, 991, 891, 760

Tripropyl butyl ammonium propionate, $[N_{3334}][OPr]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.03 (m, 8H), 2.04 (q, *J*=7.7Hz, 2H), 1.56 (m, 8H), 1.23 (hex, *J* = 7.3Hz, 2H), 0.92 (t, *J* = 7.7Hz, 3H), 0.81 (t, *J* = 7.3Hz, 12H). RMN-¹³C (400 MHz, Dmso-d₆) : δ (ppm) = 175.2, 59.2, 57.7, 31.9, 23.1, 19.2, 14.9, 13.4, 11.6, 10.5. IR v (neat, cm⁻¹): 2967, 2936, 2878, 1582, 1460, 1377, 1352, 1283, 964, 853, 758.

Tripropyl hexyl ammonium acetate, $[N_{3336}][OAc]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.02 (m, 8H), 1.76 (s, 3H), 1.54 (m, 8H), 1.19 (m, 6H), 0.81 (t, *J* = 7.3Hz, 9H), 0.74 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 172.1, 59.2, 57.8, 30.7, 26.2, 25.5, 21.9, 21.1, 14.8, 13.8, 10.5. IR v (neat, cm⁻¹): 2967, 2934, 2876, 2859, 1586, 1466, 1370, 1317, 962, 891, 760

Tripropyl hexyl ammonium propionate, $[N_{3336}][OPr]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.02 (m, 8H), 2.03 (q, *J*=7.7Hz, 2H), 1.54 (m, 8H), 1.19 (m, 6H), 0.91 (t, *J* = 7.7Hz, 3H), 0.81 (t, *J* = 7.3Hz, 9H), 0.74 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 175.1, 59.2, 57.8, 31.8, 30.7, 25.5, 21.9, 21.1, 14.8, 13.7, 11.6, 10.5. IR v (neat, cm⁻¹): 2963, 2928, 2876, 1582, 1460, 1377, 1352, 1281, 963, 853, 762.

Tripropyl octyl ammonium acetate, $[N_{3338}][OAc]$: RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.03 (m, 8H), 1.78 (s, 3H), 1.56 (m, 8H), 1.20 (m, 10H), 0.83 (t, *J* = 7.3Hz, 9H), 0.75 (t, *J* = 7.0Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆) : δ (ppm) = 172.0, 59.2, 57.8, 31.1, 28.5, 28.4, 26.2, 25.9, 22.0, 21.1, 14.8, 13.9, 10.5. IR v (neat, cm⁻¹): 2963, 2926, 2876, 2855, 1586, 1462, 1369, 1319, 990, 893, 760

Tripropyl octyl ammonium propionate, [N₃₃₃₈][OPr]:

RMN-¹H (400 MHz, D₂O) : δ (ppm) = 3.03 (m, 8H), 2.03 (q, *J*=7.7Hz, 2H), 1.55 (m, 8H), 1.19 (m, 10H), 0.93 (t, *J* = 7.7Hz, 3H), 0.83 (t, *J* = 7.3Hz, 9H), 0.77 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 176.0, 60.1, 58.7, 32.7, 32.1, 29.4, 29.3, 26.8, 22.9, 22.0, 15.8, 14.8, 12.5, 11.4 . IR v (neat, cm⁻¹): 2963, 2926, 2876, 2859, 1582, 1460, 1377, 1350, 1281, 970, 853, 760

Tripropyl decyl ammonium acetate, $[N_{33310}][OAc]$: RMN-¹H (400 MHz, D₂O): δ (ppm) = 3.05 (m, 8H), 1.78 (s, 3H), 1.58 (m, 8H), 1.21 (m, 14H), 0.85 (t, *J* = 7.3Hz, 9H), 0.79 (t, *J* = 7.0Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 172.0, 59.2, 57.8, 31.3, 28.9, 28.8, 28.7, 28.5, 26.2, 25.8, 22.1, 21.1, 14.8, 13.9 (*C*H₃), 10.5. IR v (neat, cm⁻¹): 2965, 2928, 2878, 2857, 1586, 1462, 1370, 1317, 962, 893, 760

Tripropyl decyl ammonium propionate, $[N_{33310}][OPr]$: RMN-¹H (400 MHz, D₂O): δ (ppm) = 3.05 (m, 8H), 2.04 (q, *J*=7.7Hz, 2H), 1.57 (m, 8H), 1.21 (m, 14H), 0.93 (t, *J* = 7.7Hz, 3H), 0.85 (t, *J* = 7.3Hz, 9H), 0.78 (t, *J* = 7.1Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 175.2, 59.2, 57.8, 31.7, 31.3, 28.9, 28.8, 28.7, 28.5, 25.9, 22.1, 21.1, 14.9, 13.8, 11.6, 10.5. IR v (neat, cm⁻¹): 2963, 2926, 2876, 2855, 1582, 1460, 1377, 1352, 1283, 964, 853, 756.

Tripropyl dodecyl ammonium acetate, $[N_{33312}][OAc]$: RMN-¹H (400 MHz, D₂O): δ (ppm) = 3.06 (m, 8H), 1.79 (s, 3H), 1.58 (m, 8H), 1.23 (m, 18H), 0.86 (t, J = 7.3Hz, 9H), 0.79 (t, J = 7.0Hz, 3H). RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 172.0, 59.2, 57.8, 31.3, 29.1, 29.0, 28.9, 28.8, 28.7, 28.5, 26.1, 25.9, 22.1, 21.1, 14.8, 13.8, 10.5. IR v (pur, cm⁻¹): 2965, 2928, 2878, 2857, 1586, 1466, 1371, 1317, 966, 893, 760

Tripropyl dodecyl ammonium propionate, $[N_{33312}][OPr]$: RMN-¹H (400 MHz, D₂O): δ (ppm) = 3.06 (m, 8H), 2.04 (q, *J*=7.7Hz, 2H), 1.57 (m, 8H), 1.22 (m, 18H), 0.93 (t, *J* = 7.7Hz, 3H), 0.86 (t, *J* = 7.3Hz, 9H), 0.79 (t, *J* = 7.1Hz, 3H).RMN-¹³C (400 MHz, Dmso-d₆): δ (ppm) = 175.1, 59.2, 57.8, 31.7, 31.3, 29.1, 29.0, 28.9, 28.8, 28.7, 28.5, 25.9, 22.1, 21.1, 14.8, 13.8, 11.6, 10.5.IR v (neat, cm⁻¹) : 2959, 2924, 2874, 2855, 1582, 1460, 1379, 1352, 1283, 966, 855, 762.

<u>Spectroscopy</u>: For organic compounds characterization after synthesis, IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer FTIR-8400S, equipped with a PIKE MIRacle Attenuated Total Reflectance (ATR) accessory (ATR crystal plate: germanium). For the molecular interactions study, IR spectra were recorded with a Nicolet 380 FT-IR spectrometer (DTGS detector) equipped with ATR single reflection diamond from Specac. IR spectra were averaged on 32 scans and with a resolution of 4 cm⁻¹. NMR spectra were recorded in Fourier Transform mode with a Bruker AVANCE 400 (¹H at 400 MHz, ¹³C at 100 MHz), at 298K. Data are reported as chemical shifts (δ) in ppm. Residual solvent signals were used as internal references (¹H, ¹³C).

Microscopy: In situ dissolution was followed by observing the disappearance of cellulose particles (partially crystalline) with time using a Leica DM2500M optical microscope. During the dissolution the sample is placed in between a glass slide and a glass cover in the hot stage (Linkam LTS420) in order to control temperature and atmosphere (under N₂ flow) of the sample similar to our previous work.^[16] Since the sample is not stirred during the experiment in the microscope we paid a particular attention to start the dissolution experiment with a homogeneous distribution of the cellulose particles. Cross-polarized light was used to improve the illumination of the sample by increasing the contrast between the solvent (black) and the cellulose particles (white). Images of 2048×1536 pixels are taken regularly during the dissolution experiments and represent a surface of around 4 mm² of the sample and circa $1/100^{\text{th}}$ of the total sample. A typical sample is around 40 mg which corresponds to a thickness of 100 µm. The percentages of cellulose given in this work are calculated as the ratio of (mass of cellulose) by (mass cellulose + mass ionic liquid + mass DMSO). As illustration of a typical experiment, a sample containing 10 wt% cellulose in [N₂₂₂₆][OAc] was heating at a rate of 0.25 °C/min from 30 to 80 °C. An image is taken every 2 minutes (or 0.5 °C) and few images of this experiment are given in Figure 7. All the cellulose is dissolved before the sample reaches 80 °C and most of the particles are disappearing between 50 and 60 °C. The full dissolution of cellulose was confirmed by X-ray diffraction and the absence of chemical reaction between cellulose and ionic liquid was verified by IR.



Figure 7: Images of an in situ dissolution of 10 wt% of microcrystalline cellulose in $[N_{2226}][OAc]$ from 30 °C to 80 °C with a heating rate of 0.25 °C/min. The images' size is around 2.3 mm x 1.7 mm.

The brightness of each image taken during a dissolution experiment is measured and its evolution is used to identify the temperature/time corresponding to the total dissolution of the cellulose and to compare different experiments. As example, the evolution of brightness during 3 experiments with 10 wt% of cellulose in $[N_{2226}]$ [OAc] is given in Figure 8. The brightness of the sample is systematically normalized to 100 for each experiment which does not necessary corresponds to the first image of the experiment. When the cellulose is fully dissolved the brightness of the sample is constant with a value close to 0. The brightness of the sample increases during the first few minutes. This corresponds mainly to a swelling of the cellulose particles already referred in literature.^[16, 33] Because of this, it is not possible to simply correlate the brightness of an image with the quantity of undissolved cellulose. However we can estimate that the value of the brightness is an overestimation of the quantity of undissolved cellulose. For example, with the heating rate of 2 °C/min, at 80 °C, a brightness of 20 is measured meaning that at least 80% of the initial cellulose has been dissolved.

We also observe that the temperature of dissolution is depending on the heating rate. At 2 °C/min, the cellulose is not completely dissolved before 90 °C, at 0.25 °C/min it is fully dissolved at 70 °C and at 0.01 °C/min the temperature is reduced to 52 °C (see Figure 8). At the slowest heating rate, the entire dissolution takes 1.5 days while at 0.25 °C/min it takes less than 3 hours. A heating ramp of 0.25 °C/min was used with temperatures increasing from 30 to 90 °C in order to realize an experiment in 4 hours (except in the case of ionic liquids solids at ambient temperature for which the dissolution experiments start at higher temperatures). The dissolution temperature was evaluated with a first set of experiments with a fixed quantity of cellulose (10 wt%). Experiments with different quantities of cellulose were also conducted in order to estimate the maximum quantity that can be dissolved in the ionic liquids.



Figure 8: Evolution of the brightness during the dissolution of 10 wt% of microcrystalline cellulose in $[N_{2226}][OAc]$ as observed in an optical microscope with 0.01, 0.25 and 2.00 °C/min heating ramps. Lines are connecting every experimental point (every 0.5 °C). Symbols are only here to help the reader.

<u>Characterization of regenerated cellulose</u>: In few cases, cellulose powder was precipitated from ionic liquids by addition of water and then washed 3 times. The regenerated powders are as white as the untreated cellulose. They were used to confirm the dissolution of the cellulose (strong decrease of the crystallinity of the cellulose as observed by X-ray diffractograms obtained with a Philips X-Pert Pro using Cu-K α radiation). The absence of chemical reaction of the native cellulose with the ionic liquid during the dissolution was also established (absence of C=O bands in the infrared spectra).

<u>Viscosity</u>: The viscosity of the solvents was measured using an Anton Paar Lovis 2000ME microviscometer based on the falling ball principle. A capillary tube with an internal diameter of 1.8 mm was considered optimal for viscosity up to 300 mPa.s.^[26] The density of the fluid is necessary for the calculation of the viscosity from falling ball experiments. The density of $[N_{2226}][OAc]$ (0.96063 g.cm⁻³ at 25 °C, with a linear evolution from 25 to 80 °C : density (T /°C) = 0.97436-0.0005527xT(/°C)) was measured using a vibrating tube densimeter DMA 5000M from Anton Paar. Densities for the other solvents were calculated from the density of $[N_{2226}][OAc]$ and the molar volume of CH₂ group of alkyl chain of 16.92 cm³/mol.^[34] Viscosities were measured on ionic liquids with around 0.5 wt% of water. It was considered that the measured viscosity is undervaluing the viscosity of pure ionic liquid by at least 20%.^[26]

<u>Rheology</u>: 10 wt% of cellulose has been dissolved in 0.5 g of ionic liquid within few hours at 80 °C. Rheology measurements have been performed within 24 hours after the dissolution of the cellulose in the ionic liquids in order to avoid a strong decrease of the polymer length.^[35] Melt viscoelastic experiments have been carried out with an ARES mechanical spectrometer TA Instruments in oscillatory frequency mode using parallel plates (25 mm diameter) under air atmosphere. In all cases strain amplitude has been checked to be sure to remain within the linear viscoelastic range. Temperatures of experiments ranged from 90 °C till to 30 °C. A sinusoidal strain is applied to the sample and a resulting sinusoidal stress signal is recorded. Its deconvolution between the in phase (δ =0) and the out of phase (δ = $\pi/2$) components allow the determination of the loss and storage viscosities.

<u>Molecular Simulation</u>: Molecular structures of four solvents ([N₂₂₂₄][OAc] and [N₂₂₂₆][OAc], with and without addition of DMSO) around one cellohexaose (6 glucoses units) has been calculated at 127 °C. Each simulation box was built with 1500 ions pairs, 1 cellohexaose and 0 or 637 DMSO molecules (corresponding to 20 wt% of DMSO). Simulations were performed with a time step of 2 fs in an NPT ensemble and with a cutoff of 12 Å using LAMMPS molecular dynamics code.^[36] All molecules were simulated using all-atom flexible models derived from the OPLS-AA (DMSO,^[37] cellohexaose^[38] and ionic liquids^[39]). For each solvent, 10 initial configurations were created every 200 ps in a first simulation at 427 °C. With each of these configurations, 8 cycles of (1) 400 ps at 427 °C, (2) 400 ps of equilibration at 127 °C and finally (3) 1 ns of acquisition were computed. The structure and interactions between a cellohexaose molecule and each solvent were then studied with a total trajectory of 80 ns using 80 different initial configurations in order to probe all configurations of the oligomer. The number of hydrogen bonds between anions and cellohexaose were calculated using the usual geometrical definition (distance O....H < 2.5Å and OOH angle < 30°).

Acknowledgements

We thank GDR 3585 (LIPS: Ionic Liquids and Polymers) for its financial support. The authors acknowledge Prof. Agilio Padua for his contribution in the molecular simulations.

Keyword: cellulose, ionic liquid, dissolution, polarizing optical microscopy, rheology

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