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Transition of cellulose crystalline structure in biodegradable mixtures of renewably-sourced levulinate alkyl ammonium ionic liquids, γ-valerolactone and water

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In this work, we report that combination of levulinate as a renewably sourced anion with short chain alkyl ammonium as a cation yields room temperature ionic liquids that are capable of dissolving up to 10 wt% of microcrystalline cellulose. This dissolution results in a change of the cellulose crystalline structure from cellulose I to cellulose II, a pre-requisite step known to significantly improve the accessibility of cellulose to enzymes. As compared to previous methodologies, such ILs tolerate the presence of up to 18 wt% of water. Hence technical grade ILs can be used thus avoiding the energy-consuming drying process generally required with traditional ILs before dissolution experiments. In addition, such ILs can be mixed with 20 wt% of γ-valerolactone, a renewably-sourced co-solvent, resulting in an improvement of the cellulose dissolution up to 20 wt% while concomitantly increasing the sustainability of these media. Finally, prepared ILs were proved to be biodegradable according to the OCDE 301F directive, thus opening a promising route for the pre-treatment of cellulose with a higher eco-efficiency.

Introduction

With the depletion of fossil reserves and the impact of CO_2 emissions on climate change, use of cellulose as a renewable raw material in chemical industry is gaining more and more interest for the production of various chemicals such as ethanol, solvents, monomers, surfactants, chemical platforms, etc...[1] Among the different grade of cellulose available on the market, microcrystalline cellulose (MCC) is of particular interest in fine chemistry owing to its large availability and its high content of glucose from which fuels and chemicals can be then produced. In return for this high content of glucose, MCC has a high crystallinity index. In particular, chains of MCC form two distinct allomorphs of cellulose I, I_α with a triclinic unit cell and I_β with a monoclinic cell, the fractional distribution between I_α and I_β varying according to the origin of cellulose.[2] Unfortunately, this high crystallinity of MCC hampers its accessibility to (bio)catalysts making its deconstruction difficult. To overcome this problem, MCC is generally subjected to a pre-treatment process before its (bio)catalytic deconstruction.[3] This pre-treatment aims at favouring a better accessibility of the cellulosic backbone to (bio)catalyst by modifying its crystallinity[4] or particle size[5] or degree of polymerization[6] for instance. In this context, much effort has been recently paid to the search of innovative media capable of dissolving and thus disrupting the supramolecular organization of cellulose. Dissolution of cellulose in a non-derivatizing solvent is an interesting approach that allows the cristallinity index of cellulose to be decreased or changed from cellulose I to cellulose II. In particular, cellulose II has been proved to be more readily digested by cellulases than cellulose I thanks to a decrease of the van der Waals interaction between hydrogen-bonded sheets.[7] After the dissolution process, cellulose is generally recovered by precipitation after addition of an anti-solvent such as ethanol or water.

Historically, mixtures of DMSO/LiCl or DMA/LiCl[8] (among other combinations) and *N*-methylmorpholine-*N*-oxide (Lyocell® process) have been used for the dissolution/decrystallization of cellulose.[9] Although these systems ensure a change in the crystallinity index of cellulose, their recycling is difficult and rather expensive. Recently, ionic liquids (ILs) have received considerable attentions owing to their ability to dissolve and thus to decrease the crystallinity index of cellulose.[4] Dissolution of cellulose in ILs has been firstly demonstrated at the beginning of the 20th century in particular using ethyl ammonium nitrate.[10] With the recent emergence of room temperature ILs (RTILs), the use of ILs for the dissolution of cellulose is now witnessing a sort of renaissance. Since the pioneer investigations of Rogers and co-workers,[11] plenty of works have been reported in this field of chemistry and this topic is too large to be summarized here. Complementary information to this section can be found in excellent recent reviews.[4,12]

Although elucidation of the exact mechanism governing the dissolution and change of the cellulose crystallinity in ILs is still not really clear, it has been demonstrated in the current literature that ionic liquids can provide adapted physical and chemical properties such as tunable hydrophilic–lipophilic balance and basic properties that play an important role in the dissolution

process of cellulose. It is more or less accepted that the cation has the role to slide open the cellulose fibrils and to transport the anion within the cellulose backbone where it interacts with the hydrogen bond network.[13] To date, 1-butyl-3-methyl-imidazolium chloride and 1-ethyl-3-methyl-imidazolium acetate are considered as the best ILs for the dissolution of cellulose. Despite the remarkable ability of these ILs to dissolve cellulose (up to 15-20 wt%), their industrial emergence is unfortunately hampered by their high cost, toxicity and high viscosity. Additionally, presence of water (important contaminant of biomass) is known to have a negative effect on the dissolution of cellulose in ILs. As a consequence, most of ILs requires to be dried prior to dissolving cellulose which dramatically raises their price to an unacceptable level for use on a large scale. Nevertheless, RTILs are excellent models to understand the mechanism governing the dissolution/decrystallization of cellulose.

Here we wish to report a new generation of water-tolerant ILs for the dissolution of MCC and the transition of cellulose I crystalline structure to cellulose II. In particular, we designed promising ILs for the dissolution of cellulose using various alkyl quaternary ammonium salts as cations, and levulinate as a renewably-sourced anion. We found that this specific anion greatly enhanced the rate and cellulose dissolution ability of ILs but also allows cellulose to be dissolved in the presence of up to 18 wt% of water. To our knowledge, it is the first time that
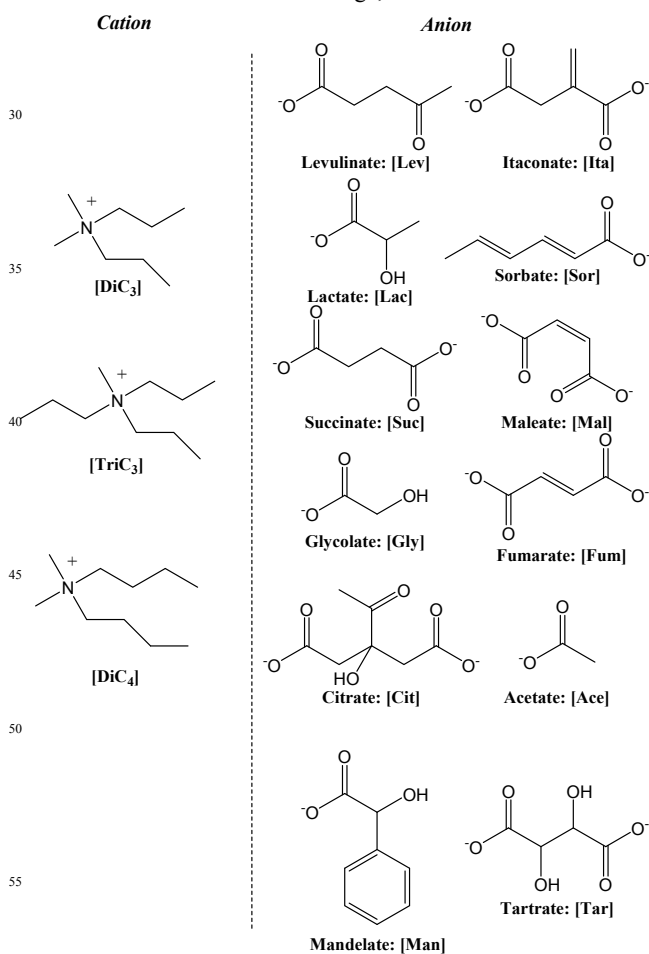
cellulose could be dissolved in a relative short time in ionic liquids containing a high amount of water, paving the way for a potential application in the industry, as water tolerance of ILs is an important bottleneck for their industrial development. In addition, these levulinate-derived alkyl ammonium ILs have been efficiently associated to 20 wt% of renewably-sourced γ-valerolactone as a co-solvent and have been proved to be biodegradable which considerably increase the attractiveness of such media for an industrial use.

Results and discussions

Procedure for the synthesis of all ILs discussed in this manuscript was inspired from previous methods. Typically, the quaternary ammonium $[(C_nH_{2n+1})_2N(CH_3)_2][X]$ or $[(C_nH_{2n+1})_3N(CH_3)][X]$ (n = 3, 4, 6; X = Br, I) salts were first prepared *via* an alkylation of *N,N,N*-alkyldimethylamines or *N,N,N*-dialkylmethylamines with 1-haloalkanes followed by an anion metathesis with OH⁻ (anion exchange over Amberlite® IRA-400) and neutralization with the desired bio-sourced acid.[14] For the sake of clarity, prepared ILs as well as their abbreviations are summarized in Scheme 1. Because

Table 1 Main physicochemical properties of prepared ILs

ILs	T_d (°C)	T_g (°C)	T_m (°C)	η /Pa·s at 25°C (80°C)	γ^a /mN·m⁻¹ at 25°C (80°C)
[DiC₃][Ace]	140-228	- 68.1	-	0.231 (0.032)	39.4 (36.2)
[DiC₃][Lac]	156-263	- 69.6	-	0.284 (0.037)	41.5 (34.1)
[DiC₃][Lev]	143-254	-13.0	-	0.194 (0.031)	34.6 (30.2)
[DiC₃]₂[Ita]	150-260	-55.3	-	1.683 (0.082)	46.8 (44.4)
[TriC₃][Ace]	140-260	-64.0	-	0.374 (0.037)	39.2 (37.2)
[TriC₃][Lac]	150-256	-68.4	-	0.196 (0.036)	42.8 (41.6)
[TriC₃][Lev]	140-250	-66.8; -11.9	-	0.218 (0.031)	35.5 (25.1)
[TriC₃]₂[Ita]	136-252	-47.4; -12.2	-	4.372 (0.099)	42.6 (39.0)
[DiC₄][Ace]	138-248	-67.8	-	0.177 (0.041)	34.7 (32.7)
[DiC₄][Lac]	162-262	-	14.6	0.428 (0.048)	37.2 (35.0)
[DiC₄][Gly]	155-272	-62.4; 0.6	-	0.585 (0.058)	41.6 (39.4)
[DiC₄][Lev]	140-258	-	-	0.172 (0.043)	36.4 (28.6)
[DiC₄][Sor]	144-245	-64.3	51.9	solid (0.064)	solid (30.6)
[DiC₄][Mand]	173-281	-52.0; -16.6	-	0.448 (0.071)	40.9 (nd)
[DiC₄]₂[Suc]	146-276	-54.7; -7.2	-	16.790 (0.307)	39.9 (40.1)
[DiC₄]₂[Ita]	142-260	-53.4; 5.4	-	0.676 (0.052)	38.6 (30.5)
[DiC₄]₂[Male]	140-250	-56.6	-	3.317 (0.092)	38.4 (37.3)
[DiC₄]₂[Fum]	153-262	-53.5; 3.1	-	2.974 (0.139)	42.3 (40.6)
[DiC₄]₂[Tar]	170-260	-36.9	-	6.525 (0.209)	30.5 (41.4)
[DiC₄]₃[Cit]	135-250	-41.8; -1.1	-	19.185 (0.316)	36.3 (36.6)

Cation

[DiC₃]

[TriC₃]

[DiC₄]

Anion

Levulinate: [Lev]

Itaconate: [Ita]

Lactate: [Lac]

Sorbate: [Sor]

Succinate: [Suc]

Maleate: [Mal]

Glycolate: [Gly]

Fumarate: [Fum]

Citrate: [Cit]

Acetate: [Ace]

Mandelate: [Man]

Tartrate: [Tar]

Scheme 1 List of ILs prepared in this work

some of prepared ILs are not described in the current literature, the list of the main physicochemical properties of ILs is provided in Table 1. The phase transitions of prepared ILs were determined by differential scanning calorimetry (DSC). Except for
5 [DiC$_4$][Sor] which exhibits a melting temperature of 51.9°C, all other prepared technical grade ILs are liquid at room temperature (see water content in table 2). The glass transition (T_g) and the melting temperature (T_m) of all ILs are provided in Table 1.[15, 16] Thermogravimetric analysis (TGA) was carried out to determine
10 the decomposition temperature and therefore the thermal stability of the prepared ILs. For all compounds, thermal decomposition occurred between 140 and 170 °C. Note that viscosity (η) and surface tension (γ) of prepared ILs are discussed later in the manuscript.

15 **Dissolution ability of prepared ILs**

All cellulose dissolution experiments were performed using a microcrystalline cellulose (MCC) of the type AVICEL PH 200. AVICEL PH 200 has a glucose content higher than 99% along with a degree of polymerization of 200, a particle size of 150 µm
20 and a water content of 5 wt%. In a typical experiment, a solution of IL containing 2 wt% of MCC was heated at 90-115°C. When MCC was dissolved, then extra amount of MCC was progressively added up to the limit of solubility was reached.

Table 2. Dissolution of cellulose in prepared ILs

Anion	Cation	Water content (wt%)	Dissolution (wt%)	Dissolution rate (g/h)
[Lev]	[TriC$_3$]	3.5	10	5.0
	[TriC$_3$]	15.5	10	5.0
	[DiC$_4$]	2.5	10	2.0
	[DiC$_4$]	14	10	2.0
	[DiC$_3$]	2.6	10	2.0
	[TriC$_4$]	6.7	5	1.7
[Ita]	[DiC$_4$]	12.8	10	1.4
	[DiC$_3$]	5.9	6	0.9
	[TriC$_3$]	8.3	0	-
	[TriC$_4$]	6.6	0	-
[Ace]	[DiC$_4$]	10.8	9.5	2.4
	[DiC$_4$]	16.8	9.5	1.3
	[TriC$_4$]	6.5	2.6	0.4
	[DiC$_3$]	10.0	0	-
	[TriC$_3$]	7.7	0	-
[Lac]	[DiC$_4$]	2.8	3.3	1.7
	[TriC$_3$]	2.6	0	-
[Sor]	[DiC$_4$]	5.5	2	0.7
[Suc]	[DiC$_4$]	5.3	2	0.2
[Cit]	[DiC$_4$]	7.3	2	0.1
[Gly]	[DiC$_4$]	5.0	0	-
	[TriC$_4$]	1.6	0	-
[Man]	[DiC$_4$]	1.1	0	-
[Mal]	[DiC$_4$]	11.5	0	-
[Fum]	[DiC$_4$]	9.8	0	-
[Tar]	[DiC$_4$]	4.1	0	-

25 ^{a} dissolution experiments were performed within a range of temperature of 90-110°C.

Considering that the total removal of water from ILs is a costly and energy consuming step, we decided here to not extensively dry ILs prior to dissolving cellulose and to evaluate their
30 performances as collected after synthesis. Results on solubility measurements are summarized in table 2. Among all tested renewably-sourced anions, it appears that levulinate is the most promising one allowing up to 10 wt% of MCC to be dissolved within only 2h of stirring at 90°C. In a first approximation,
35 efficiency of anions for cellulose dissolution can be classified as follow levulinate>itaconate, acetate>lactate>sorbate, succinate, citrate>glycolate, mandelate, maleate, fumarate, tartrate. As a general trend, it appears that anions bearing a hydroxyl group such as tartrate, citrate, mandelate, glycolate and lactate are not
40 favourable for the dissolution of cellulose. Presence and substitution of a carbon-carbon double bond on the structure of anions also exerted an influence on the cellulose dissolution. Whereas anion with disubstituted C=C bond such as maleate and fumarate are incapable of dissolving cellulose, 10 wt% of
45 cellulose can be dissolved in the presence of itaconate which exhibit a terminal C=C bond.

For all eligible anions, it is noteworthy that difference of dissolution ability was obviously observed according to the nature of the cation confirming that the cation does also
50 participate to the dissolution mechanism. Except levulinate which was able to dissolve rather large amount of cellulose whatever the cation, the [DiC$_4$] cation afforded the best result in terms of both dissolution ability and dissolution rate for all tested anions.

As mentioned above, water contained in commonly used
55 imidazolium-derived ILs has an inhibiting effect on cellulose dissolution thus requiring an extensive and energy-consuming drying of ILs before dissolution experiments. In this context, the water content of prepared ILs and its effect on the cellulose dissolution has been investigated (Table 2). The water content of
60 each ILs was determined by means of Karl-Fischer titrations. Most of ILs contains water within a range of 1.1-12.8 wt%. Although [TriC$_3$][Lev] (the best ILs in term of dissolution ability and rate) has a lower water content than the average of tested ILs, there is no clear relationship between the water content of ILs and
65 their ability to dissolve cellulose. For instance, [DiC$_4$]$_2$[Ita] and [DiC$_4$][Ace] exhibited a high water content of 12.8 and 10.8 wt%, respectively, and are capable of dissolving 10 and 9.5 wt% of cellulose whereas with a similar water content [DiC4]$_2$Mal and [DiC$_4$]$_2$[Fum] are not able to dissolve cellulose (Table 2). These
70 results suggest that the dissolution of cellulose is more depending on the molecular structure of the alkylammonium carboxylate ILs than on the water content of ILs.

Considering that the water-tolerance of the best ILs *i.e.* [TriC$_3$][Lev] and [DiC$_4$][Ace] is a remarkable advantage over
75 imidazolium-derived ILs, we then checked their ability to dissolve cellulose when the water content was increased (Fig. 1, Table 2). Remarkably, we were pleased to see that [TriC$_3$][Lev] and [DiC$_4$][Ace] were still able to dissolve similar amount of cellulose (10 wt% and 9.5 wt%, respectively) at a water content
80 of 15.5 wt% and 16.8 wt%, respectively. Interestingly, in the case of [TriC$_3$][Lev], the dissolution rate of cellulose was not affected by the presence of water whereas it was the case with [DiC$_4$][Ace] for which an increase of the water content from 10.8 wt% to 16.8 wt% dramatically reduced the cellulose dissolution
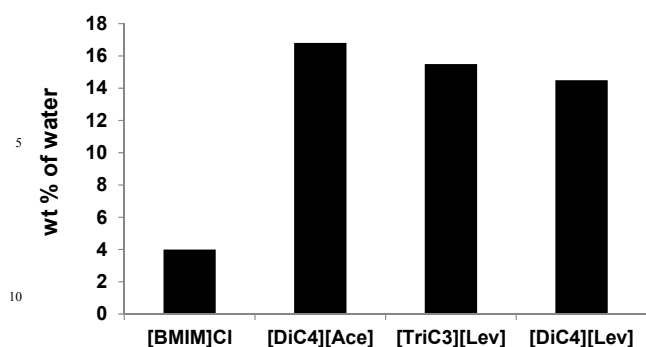
Fig 1. Water-tolerance of tested Ils (results collected at 90°C).

rate from 2.4 g/L to 1.3 g/L (Table 2). Note that in both cases, cellulose was not dissolved anymore when the water content was
15 higher than 18 wt% which represents here the maximum tolerance of these ILs to water. When [BMIM]Cl was used as a reference IL, we found that a water content higher than 4 wt% totally inhibited the dissolution process showing the remarkable efficiency of [TriC$_3$][Lev] and [DiC$_4$][Ace] in the dissolution of
20 cellulose. Note that similar conclusion can be drawn with the [DiC$_4$][Lev] IL that can dissolve up to 10 wt% of cellulose at a water content of 14 wt% (similar dissolution rate =2g/h, table 2).

The temperature obviously plays also a pivotal role on the ability of ILs to dissolve cellulose. Similarly to common ILs such as
25 [BMIM]Cl (solid up to 70°C) or [BMIM]Ace (RTIL), below 70°C no dissolution occurred. The dissolution process started at 70°C and was complete only at a temperature within the range of 90-110°C.

At this stage one may conclude that the [TriC$_3$][Lev] IL appears
30 as a promising ILs for the dissolution of cellulose. In particular, the tolerance of [TriC$_3$][Lev] to water is a noticeable advantage over imidazolium-derived ILs for use on a large scale.

Physicochemical properties of ILs

To better understand the difference of dissolution ability observed
35 between the alkylammonium ILs, we then focused on the viscosity (η) and surface tension (γ) of ILs.

Viscosity is an important physical property considering the application of ILs because of its strong effect on the rate of mass transport.[17, 18] Because dissolution experiments were performed at
40 80-110°C, the variation of the viscosity *versus* temperature was investigated over a temperature range of 25 to 80 °C for the different ILs. As expected, the viscosities decreased with an increase of the temperature. However, at 80°C, one should notice that most of ILs exhibit viscosities in a similar range (0.030-0.099
45 Pa·s). Only [DiC$_4$]$_2$[Suc], [DiC$_4$]$_2$[Tar] and [DiC$_4$]$_3$[Cit] exhibited a slightly higher viscosity at 80°C (0.2-0.3 Pa·s). Hence, one may conclude that viscosity of ILs is not a good descriptor to explain the greatest ability of levulinate-derived ILs to dissolve cellulose.

Next, we focused on the surface tension which provides
50 information on the cohesive forces between liquid molecules at the surface.[19] All prepared ILs have higher surface tensions than most of common molecular solvents (*e.g.* ethanol: 22.0, acetone: 23.5, diethyl ether: 16.6 mN·m^{-1}), but lower than water (72 mN·m^{-1} at 25 °C) (Table 1). Generally, the surface tension at the
55 liquid/air interface decreases with an increase of the temperature as a result of the change of the internal cohesive energy (sum of
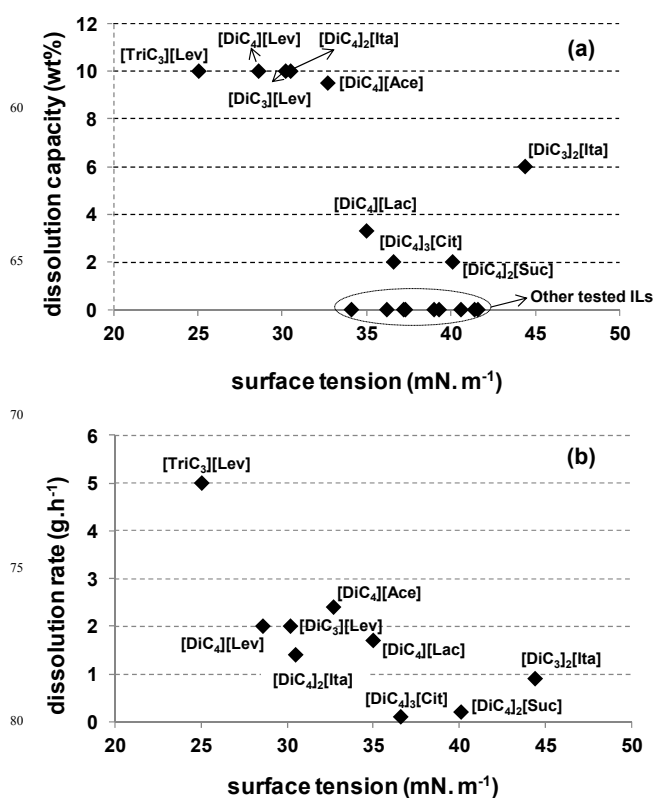

Fig. 2 Relationship between the surface tension of ILs at 80°C and (a) their cellulose dissolution ability and (b) cellulose dissolution rate

85 molecular interactions, like electrostatic and van der Waals interactions).[19] All of the investigated ILs show this expected behavior: the reduction of the surface tension values at high temperature is noticeable and the temperature effect is averagely the same for the different ILs (Table 1). **Although surface**
90 **tension of ILs is far to be the only parameter governing the dissolution of cellulose**, we experimentally observed a relationship between the ability of ILs to dissolve cellulose and their surface tensions measured at 80°C. As a general trend, the dissolution of cellulose in ILs is higher for ILs exhibiting the
95 lowest surface tension ([DiC$_3$]$_2$[Ita] is the only exception). In particular, whatever the cation ([DiC$_4$], [DiC$_3$] or [TriC$_3$]), we noticed that ILs exhibiting a surface tension lower than 35 mN m^{-1} dissolved the highest amount of cellulose (Fig. 2a). The same trend was also observed on the dissolution rate of cellulose *i.e.*
100 the lowest the surface tension, the highest the dissolution rate (Fig. 2b). In a first approximation, one may hypothesize that ILs with a low surface tension (main feature of levulinate-derived ILs) has a low cohesive energy and are thus more prone to interact with the hydrogen bond network of cellulose.

105 ### Contribution of GVL as a renewable-sourced co-solvent

In order to bench-mark the levulinate to the chloride anion, we then compared the ability of [DiC$_4$][Lev] and [TriC$_3$][Lev] to dissolve cellulose with that of [DiC$_4$]Cl and [TriC$_4$]Cl. Comparison was also carried out with the well-known [BMIM]Cl
110 often used as a reference in the current literature. Results are summarized in table 3.

[TriC$_4$]Cl and [BMIM]Cl are capable of dissolving similar

amount of cellulose (10 wt%) to [TriC$_3$][Lev] and [DiC$_4$][Lev] while the solubility of cellulose in [DiC$_4$]Cl is much lower (3.5 wt%). Difference of dissolution rate was however clearly observed between chloride and levulinate-derived alkyl ammonium ILs (only [BMIM]Cl approached the performances of [TriC$_3$][Lev]). In particular, dissolution of cellulose in levulinate-derived alkyl ammonium ILs is faster than in chloride-derived alkyl ammonium ILs. For instance, the dissolution of cellulose is 8 times faster in [TriC$_3$][Lev] than in [TriC$_4$]Cl (Table 3, entries 1, 3). This result might be here ascribed to the high viscosity of chloride-derived alkyl ammonium ILs (solid at room temperature) as compared to [TriC$_3$][Lev] and [DiC$_4$][Lev] (RTILs) making the stirring of the solution rather difficult. For instance, using [TriC$_4$]Cl, we noticed that a gel was rapidly formed after the progressive addition of cellulose which obviously impacts not only the dissolution rate but also the cellulose dissolution ability of [TriC$_3$]Cl. This effect is even more pronounced using [DiC$_4$]Cl. Whereas [DiC$_4$]Cl dissolved cellulose at a higher rate than [TriC$_3$]Cl, only 3.5 wt% of cellulose can be dissolved in such IL. Here again, the system is limited by the formation of a highly viscous gel during the dissolution process that prevent the stirring of the mixture and thus the dissolution of a larger amount of cellulose. To circumvent this problem, the [DiC$_4$]Cl was diluted with an organic solvent to overcome mass transfer limitation. Although dimethylsulfoxide can be used as non protic polar organic solvent to fluidify the system, we focused our attention on the use of γ-valerolactone (GVL), a sustainable chemical derived from levulinic acid.[20] Interestingly, addition of GVL to the [DiC$_4$]Cl IL helped not only to fluidify the medium but also to increase the cellulose dissolution ability of [DiC$_4$]Cl. In particular, in a mixture [DiC$_4$]Cl/γ-valerolactone (15/1 *i.e.* 18 wt% of γ-valerolactone), 10 wt% of cellulose with a dissolution rate of 3.3g/h was observed *vs* 3.5 wt% at a rate of 1.6 g/h without assistance of GVL (Table 3, entries 4, 6). Note that a higher content of GVL led to a decrease of the dissolution ability of the mixture. Promoting effect of GVL on the dissolution of cellulose was then checked using [TriC$_3$][Lev]. Remarkably, using GVL as a co-solvent (20 wt%) allowed also the dissolution ability of [TriC$_3$][Lev] to be improved from 10 wt% to 20 wt% while the dissolution rate remained constant (5 g/h) (Table 3, entry 7). It is worth noting that this is one of the highest dissolution capacity ever reported for ILs demonstrating the efficiency of the proposed system. One should comment that after regeneration of cellulose (see procedure below), analysis of the reaction medium by ^{1}H NMR revealed than GVL remained unaltered and may be thus recycled. In addition, IR spectrum of regenerated cellulose

did not reveal the presence of carbonyl group further confirming the chemical inertness of GVL in our conditions (Fig. S1).

Regeneration of cellulose and recycling experiments

Next, we have investigated the regeneration of cellulose. In this study, [TriC$_3$][Lev] was selected. Same experiments were also conducted with [TriC$_4$]Cl to show the beneficial effect of the levulinate anion (as compared to the chloride anion) on the regeneration of cellulose. By means of TGA analyses, we found that these two ILs are stable up to 140-150°C which should also facilitate their long term recycling. Once dissolved, cellulose was regenerated from the IL by precipitation with addition of an anti-solvent which is generally ethanol, water or acetone as described in the current literature. Whereas in the case of [TriC$_4$]Cl, more than 95 wt% of cellulose was conveniently recovered by addition of acetone, water or ethanol, all attempts to recover cellulose from the [TriC$_3$][Lev] using acetone or ethanol failed mainly due to the very high solubility of cellulose in this system. Use of an excess of water was however found much more efficient to regenerate cellulose from [TriC$_3$][Lev]. In particular, addition of 10 mL of water to 1.5 g of [TriC$_3$][Lev] containing 10 wt% of cellulose led to more than 95 wt% of recovery of cellulose.

XRD analyses of regenerated cellulose (from [TriC$_3$][Lev]) confirmed that its dissolution/regeneration led to a change of its crystallinity index from 74% to 64%. XRD patterns of AVICEL PH 200 (cellulose I) is composed of three peaks.[21] The main peak observed at 22.5° corresponds to the distance between hydrogen-bonded sheets. Additionally, a broad peak located at ~ 16° (overlap of two peaks resulting from the contribution of I$_\beta$ and I$_\alpha$) is also observed together with a third peak at 34.5° stemming from the ordering along the fiber direction. After dissolution/regeneration of cellulose I (MCC) in [TriC$_3$]Lev, XRD analyses revealed that cellulose II was obtained which is typically characterized by a broad peak at 12.1° and two main peaks at 20.5° and 22.0° (Fig. 3).[22] Change in the crystallinity from cellulose I to cellulose II was also typically observed using the mercerization process[23] or the treatment of MCC in subcritical water[24] or ball-milling in the presence of water.[25]
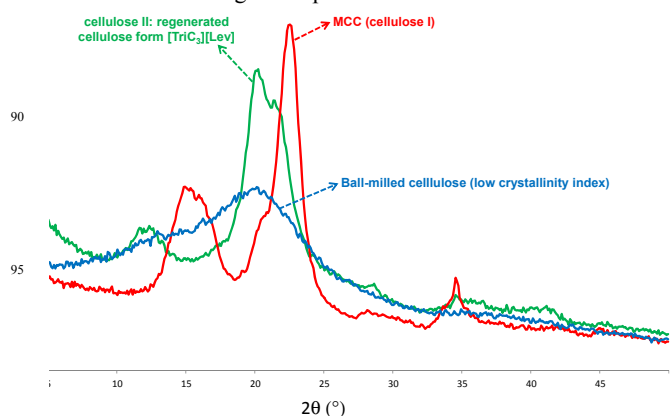

Fig. 3 XRD patterns of MCC (cellulose I), regenerated cellulose from [TricC$_3$][Lev] (cellulose II) and ball-milled cellulose ("amorphous" cellulose)

The change of cellulose crystalline structure from I to II was also confirmed by ^{13}C CP/MAS NMR (Fig. S5).[26] It should be noted that ^{13}C CP/MAS NMR also confirmed the slight decrease in

Table 3. Comparison of levulinate anion with chloride anion

Entry	ILs	T (°C)	wt % dissolution	Dissolution rate (g/h)
1	[TriC$_3$][Lev]	90	10	5
2	[DiC$_4$][Lev]	90	10	2
3	[TriC$_4$]Cl	110	10	0.6
4	[DiC$_4$]Cl	115	3.5	1.6
5	[BMIM]Cl	90	10	4
6	[DiC$_4$]Cl/GVL	100	10	3.3
7	[TriC$_3$][Lev]/GVL	90	20	5
8	GVL	100°C	-	-

crystallinity when changing cellulose I (MCC) to II. However, crystallinity values determined by NMR are lower than those determined by XRD (54% for cellulose I and 45% for cellulose II) which is also typically observed in current literature.

Regeneration of cellulose II after the pre-treatment of MCC in [TriC$_3$][Lev] is of huge interest for industrial application since cellulose II is known to be more readily digested than MCC or "amorphous" cellulose (commonly obtained by dry ball-milling), thus increasing again the attractiveness of such ILs.[2]

On the other hand, FT-IR of regenerated cellulose II was very similar to that of MCC (cellulose I) suggesting that glucose units were not damaged or functionalized during the dissolution process (Fig. S1). The surface area and porous volume was also determined. Although a slight increase of the porous volume and surface area was observed after the dissolution/regeneration process, it should be however noted that results were within the uncertainty of measurements and thus were not included in this manuscript. Finally, viscosimetry analyses revealed that the degree of polymerization of cellulose remained unchanged after the dissolution process.

After removal of the anti-solvent, the recycling of [TriC$_3$][Lev] and [TriC$_4$]Cl was then attempted. Curiously, in the case of [TriC$_4$]Cl, no dissolution occurred in the second cycle when cellulose was regenerated either with water or ethanol as an anti-solvent. Analysis of the used [TriC$_4$]Cl by ^{1}H NMR (in DMSO-d6) revealed that the chemical structure of the IL was preserved during the dissolution process. However, we noticed by ^{1}H NMR that it was very difficult to fully remove water or ethanol from the used [TriC$_4$]Cl, even when freeze-drying was employed (Fig. S2). We suspect that the difficulty to remove ethanol from [TriC$_4$]Cl may be attributed to the formation of deep eutectic or azeotropic mixture between ethanol as a hydrogen bond donor and [TriC$_4$]Cl as a hydrogen bond acceptor. At this stage we have however no evidence to support this hypothesis. To confirm the negative effect of ethanol on the dissolution of cellulose, [TriC$_4$]Cl was first dissolved in ethanol which was then removed under vacuum prior to dissolving cellulose. After this treatment, all attempts to use [TriC$_4$]Cl in the dissolution of cellulose failed supporting the inhibiting effect of ethanol in the dissolution of cellulose. When a non protic polar solvent such as acetone was used as an anti-solvent instead of water or ethanol, [TriC$_4$]Cl was successfully recycled at least four times without appreciable decrease of its dissolution ability further demonstrating the "poisoning effect" of protic solvents such as ethanol and water during the recycling experiments of [TriC$_4$]Cl. These results suggest that use of polar protic solvents to regenerate cellulose from [TriC$_4$]Cl is detrimental for its recyclability which represent a serious limitation to the use of this IL.

Conversely, as mentioned above, [TriC$_3$][Lev] is tolerant to presence of water. Thereby, recyclability of this levulinate-derived IL is not affected by water and can be thus successfully recycled at least 4 times without intermediate purification (Fig. S3 for ^{1}H NMR spectrum of reused [TriC$_3$][Lev]. Note that NMR analysis of used [TriC$_3$][Lev] confirmed its stability.

Biodegradability

Biodegradability is a key parameter in the hazard assessment of chemicals. When new industrial chemical products are developed, the question of sustainability is a major concern. High biodegradability is thus required to reduce bioaccumulation or persistence in the environment and to limit any possible adverse effects. Biodegradation tests were performed following the OECD 301 F procedures (Organisation for Economic Cooperation and Development OECD, 2006) by measuring the oxygen uptake.

Although the tolerance of tested ILs to the presence of water and GVL definitely contributes to increase the sustainability of this system, we then evaluated the impact of the anion on the biodegradation of ILs which is one of the main obstacles that

Table 4. Biodegradation of selected ILs

| Entry | ILs | % Biodegradation | | wt% of the anion |
		10 days	28 days	
1	[DiC$_4$]Cl	5	5	-
2	[DiC$_4$][Ace]	65	77	28
3	[DiC$_4$][Lev]	21	66	42
4	[DiC$_4$]$_2$[Ita]	36	45	29
5	[DiC$_4$][Lac]	41	72	36
6	[DiC$_4$]$_3$[Cit]	65	69	29
7	[DiC$_4$][Sor]	16	54	41
8	[DiC$_4$]$_2$[Suc]	65	69	43

current ILs are facing. Biodegradation is defined as the weight percent of ILs converted to CO_2 after 10 and 28 days. For the sake of clarity, the [DiC$_4$] cation has been selected in these experiments. Results are summarized in table 4. As expected, in the presence of a Cl$^-$ anion, the corresponding ILs exhibited a poor biodegradability which is also consistent with previous reports on [BMIM]Cl. However, presence of a renewably-sourced anion greatly enhanced the biodegradation of ILs. After 28 days, biodegradation of renewably-derived ILs can be classified as follows [DiC$_4$][Ace]> [DiC$_4$][Lac]> [DiC$_4$]$_3$[Cit] and [DiC$_4$]$_2$[Suc]>[DiC$_4$][Lev]> [DiC$_4$][Sor]> [DiC$_4$]$_2$[Ita]. Interestingly, we observed that the anion is not the only part of the IL to enter into the biodegradation process. In particular, we noticed that the anion also exerted an influence on the biodegradation of the quaternary ammonium cation. Indeed, if one may consider that only the renewably-sourced anion is biodegraded, then the biodegradability would have followed the wt% proportion of the anion in the IL (Table 4). For most of investigated ILs in our study, the biodegradation exceed the wt % of the anions, implying that the cation is concomitantly biodegraded. In particular, this is clearly highlighted by the good biodegradation of [DiC$_4$][Ace] keeping in mind that the reference material of the test is sodium acetate (Table 4, entry 2). In the literature, very few studies or data are available on the biodegradation of organic acid-derived quaternary ammonium. The short set of data available attest that the biodegradation of the ammonium cation is also obviously depending on the cation structure (such as the number of methylene group or the length of some alkyl groups)[27] but also on the absence of toxicity generated by the biodegradation of the anions. According to the OCDE 301F directive, [DiC$_4$][Lev] and [DiC$_4$][Ace] are thus considered as biodegradable solvent further increasing the sustainability of these systems.

B experimental

Dissolution of cellulose: In a typical experiment, 1.5 g of IL (or mixture of the IL with GVL or water) was first heated under

stirring in a sealed glass vial at the desired temperature (see Table 2). Then, 2 wt% of cellulose AVICEL PH200 was added into the IL and the heating time was prolonged up to complete dissolution of cellulose was observed. When cellulose was completely dissolved, extra amounts of cellulose were then progressively added up to the limit of solubility was reached. Please note that cellulose needs to be added progressively otherwise dissolution ability of ILs are lower. ILs that are unable to dissolve at least 2 wt% of cellulose within 10h of heating were considered as not efficient.

Please note that all attempts to dissolve wheat straw or poplar wood in such ILs failed indicating that use of these ILs is at the moment only restricted to cellulose.

Regeneration of cellulose: After complete dissolution of cellulose in the IL, cellulose was regenerated by addition of an antisolvent, preferentially water when using levulinate-derived ILs. In a typical procedure involving [TriC$_3$][Lev], 10 mL of water was added to the hot solution of [TriC$_3$][Lev] (1.5 g) containing 10 wt% of cellulose. Note that for some of ILs described in the manuscript (mostly chloride-derived ILs), acetone or ethanol were also used to regenerate cellulose. The regenerated cellulose was then filtered off and successively washed with water and acetone to remove residual ILs. Crystallinity and degree of polymerization of regenerated cellulose was then checked by XRD and FTIR analyses, respectively.

Recycling of cellulose: After regeneration and filtration of cellulose II, water was removed under reduced pressure. Then, the recovered IL was directly reused without any further purification using the same procedure as described above for dissolution experiments. Although tested ILs were recycled at least five times without appreciable decrease of their dissolution ability, we would like to point out that the long term recycling of ILs is more problematic like it is also observed with imidazolium-derived ILs (accumulation of impurities stemming from the slight degradation of cellulose).

Conclusions

Here we report that the use of levulinate as a renewably-sourced anion allowed designing various technical grade room temperature short chain (C$_3$ and C$_4$) alkyl ammonium-derived ILs that are capable of dissolving cellulose AVICEL with a high efficiency. In particular, best systems are capable of dissolving up to 20 wt% of cellulose at a dissolution rate of 5g/h which is among the highest dissolution capacity reported in the current literature. After regeneration, the crystalline structure of MCC was changed from I to II, a key point known to improve the digestibility of cellulose by cellulases. Although the concept of cellulose derystallization in ionic liquids is known, it is our opinion that our work offers significant scientific breakthroughs in this field of chemistry as compared to the previous methodologies such as (1) their tolerance to the presence of up to 18 wt% of water which is one of the main drawbacks that common ILs are currently facing for use of on a large scale, (2) their tolerance to the presence of 20 wt% of GVL as a renewably-sourced co-solvent and (3) their biodegradability which dramatically increase the eco-efficiency of these systems.

Among the different combination, a mixture composed of technical grade [TriC$_3$][Lev] and 20 wt% of GVL afforded similar results in terms of both dissolution ability and dissolution rate than imidazolium-based IL. Combination of levulinate to other cations as well as evaluation of these mixtures in lignocellulosic biomass pre-treatment is now under investigations in our groups.

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Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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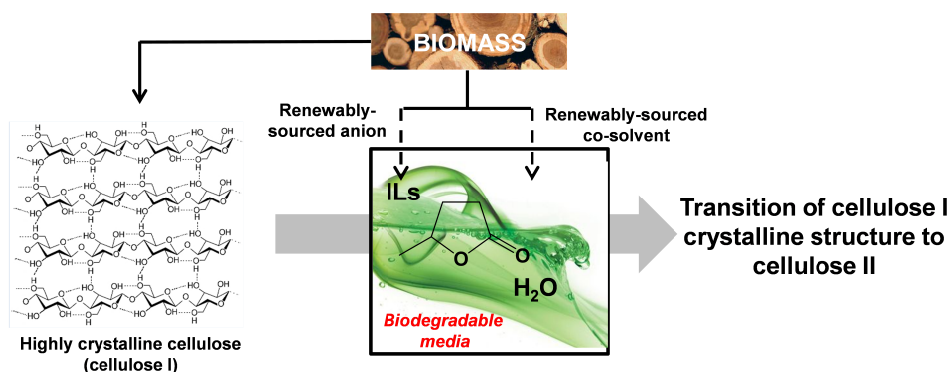
ARTICLE TYPE

Graphical abstract

Transition of cellulose crystalline structure in biodegradable mixtures of renewably-sourced levulinate alkyl ammonium ionic liquids, γ-valerolactone and water

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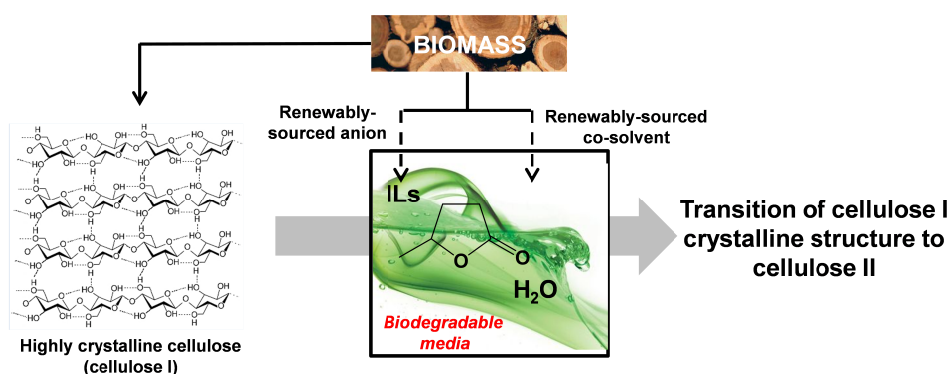
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