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### New Dual Functionalized Zwitterions and Ionic Liquids; Synthesis and Cellulose Dissolution Studies

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#### **Abstract:**

New dual functionalized *N*-oxyethylene-*N*-sulfopropyl imidazolium based ionic liquids (ILs) with unconventional anions for cellulose dissolution were synthesised and characterised (NMR, IR, HRMS, TGA,  $T_d$ ). The ILs were applied in studies on cellulose (MCC) dissolution. Results showed that varying the IL cation had greater impact on cellulose dissolution ability than the minor effect seen by anion exchange. Up to 20 wt-% MCC was dissolved in DMF/ILs solutions at 100°C. The dual functionalized ionic liquids (ILs) were synthesized via the corresponding *N*-oxyethylene imidazolium sulfonate zwitterions (ZIs), which were prepared (74-99%) through a double *N*-imidazole alkylation procedure, including 1,3-propanesultone ring opening. The original MCC and the regenerated cellulose samples were characterized by XRD analysis.

Keywords: cellulose dissolution, new ionic liquids, IL synthesis

#### 1. Introduction

The search for renewable technologies replacing fossil sources of carbon is important in the quest of a sustainable future. Biomass is the only renewable organic carbon resource in nature [1], and has a great potential for conversion into valuable chemicals and biofuels. Lignocellulose biomass comes from woody and herbaceous plants and represents the most abundant form of plant material. Such biomass represents resources that would not compete with food production. The cellulose (30-50 wt-%) in lignocellulose has, however, high chemical and mechanical stability, and is insoluble in water and most common organic solvents [2], since the cellulose strands in lignocellulose consists of polyglucose units connected through complex intra- and intermolecular hydrogen bonds (Figure 1), forming stacked layers.

Cellulose in its native state, cellulose I, is more recalcitrant than its regenerated forms, cellulose II [3, 4]. A promising strategy for production of biofuels is therefore cleavage of the intermolecular hydrogen-bonds of cellulose in order to separate cellulose into the individual polyglucose chains, which can easily be further broken down by microbial fermentation or enzymatic treatment [5] for production of bioethanol. However, it is challenging to develop methods to break down the cellulose efficiently in an environmentally friendly way. Ionic liquids (ILs) were reported to be used for dissolution of cellulose in 2002 [6]. ILs are organic salts consisting of cations and anions. Because of their special properties, such as high thermal stability, low vapour pressure, intrinsic ionic conductivity etc, they find applications in various fields such as separation, electrolyte for batteries, organic synthesis etc.[7-14] Comprehensive investigations on ILs for cellulose dissolution has later given important experience and contributed to development of the field. Cellulose has been dissolved in a number of ILs in various degree [2] typically 5-20 wt-% [5]. The cellulose single poly-glucose chains, regenerated by addition of water or protic organic solvents [5] can be used in biofuel production. Resent up-dates on topics relevant for cellulose IL dissolution, such as properties of the hydrogen bonds in ILs[15] and development of materials based on regenerated cellulose, [16] have been summarized. In addition, subjects like nuclear understanding of IL cellulose dissolution [17] and recent progress and future perspectives of imidazolium-based ILs [18] have been highlighted and reviewed.

The IL dissolution of cellulose takes place by cleavage of the intermolecular hydrogen-bonds by competing formation of electron donor-electron acceptor complexes with the cation and anion of the IL [2] (Figure 1). It is

known that both the IL cations and anions influence the dissolution of cellulose. The anions seem to play a more dominant role, and the trends in dissolution seem to follow anion basicity to cause strong H-bond accepting capacity [19]. The role of the cation is less clear, but proton acidity and functional groups in the cations are crucial for cellulose dissolution. The cation size may affect the dissolution ability, as cations with bulky groups may create unwanted steric hindrance. Thus, smaller alkyl substituents seem to facilitate dissolution [18]. ILs with cations based on commercially available imidazolium structures are promising for cellulose dissolution [2]. ILs with cations such as methylimidazolium or methylpyridinium with allyl-, ethyl-, or butyl-side chains, combined with anions, limited to acetate, chloride, and formate [19],[20],[21], are reported to be efficient in dissolving cellulose [2]. Incorporation of highly electronegative atoms such as oxygen is reported to decrease the proton acidity and thereby the solvation effect [22]. However, it is reported that poly(ethylene glycol)functionalized ILs are capable of dissolving 8-12 wt-% cellulose [23].



Figure 1. Postulated dissolution of cellulose polyglucose chains with imidazolium based ILs (X<sup>-</sup> anion).[2]

The ideal ILs for cellulose dissolution are characterized with some additional properties, such as low viscosity, low toxicity and high thermal stability [2]. Also, such ILs should be readily recyclable [24]. The increase in viscosity that occurs upon dissolution of the cellulose in ILs can cause problems [25, 26] like inefficient stirring and low dissolution rate [2]. Significant decrease in viscosity are obtained by addition of polar aprotic solvents, such as DMSO and DMF [27-31], to the dissolution process, allowing vigorous stirring and faster dissolution by enhanced mass transport [31]. The cellulose does not dissolve in pure polar solvents but is soluble in IL/organic solvent solutions. It has been proposed that polar aprotic solvents like DMSO contribute by solvation of the IL cations to leave the respective anions more available for interaction with the H-bonds of cellulose [29].

It is important to consider the toxicity when designing new ILs for cellulose dissolution. The cation nature may affect the toxicity, and ILs [32], particularly based on imidazolium, are relatively toxic, mostly as a function of the alkyl chain length of the cation [32]. However, toxicity of ILs may be altered by design. The toxicity of imidazolium based ILs can be reduced by introducing hydroxyl and ether functionalities [33] in the imidazolium side chains. Alternatively, zwitterionic heterocyclic structures ZIs [32] can be formed by incorporation of polar anions, such as sulfonate [34],[32] or carboxylate, [35] at the end of the alkyl chain of the imidazolium cation [36]. The respective ILs can be made by ZI protonation. SO<sub>3</sub>H-functionalized ILs have showed higher dissolution activities than non-functionalized ILs [37].

Substituents with repeating ethylene oxide units may both reduce the ILs toxicity [8, 33] and the melting points of ZI to give zwitterionic (ZILs) [34], liquid at room temperature. Therefore, low-melting *N*-oxyethylene imidazolium sulfonate zwitterions, such as **5b** and **8b**, [34] have been prepared by incorporation of *N*-oxyethylene units and subsequent alkylation by 1,3-propanesultone ring-opening (Scheme 1) [32, 34]. *N*-Oxyethylene imidazolium carboxylate ZIs [35] are reported, as well. From the described ZIs, less-toxic ILs can be made by protonation with addition of a strong acid. Conventional preparation of imidazolium based ILs mainly proceeds through imidazole *N*-quarternization with alkyl halide to give imidazolium halides. The desired anions are introduced by final counter-ion exchange. Thus, the preparation method via ZIs enable simple synthesis of ILs with less conventionally used anions, different from OAc, Cl and formate. Additionally, as the method does not require anion exchange, problems with halide impurities in the final IL products used for cellulose dissolution are eliminated.

The present state-of the-art is that some OAc imidazolium based ILs have reached a capacity of up to 20 wt-% cellulose dissolution [19]. In order to develop the IL concept into an industrial cellulose dissolution method, previous reports conclude that design of next generation ILs with higher dissolving capability is of importance.

In our study, the synthesis of a series of new dual functionalized ILs by the alternative ZI pathway is described. ILs based on *N*-oxyethylene-*N*-sulfopropylimidazolium cations were prepared via the respective *N*-oxyethylene imidazolium sulfonate ZIs. The desired ILs, with less frequently used counter-anions for cellulose dissolution, were obtained by final protonation of the respective ZIs with the appropriate acid (Scheme 1). The properties of the new ILs and their ability to dissolve cellulose in a mixed solution with a polar solvent are discussed. Recent reports suggest that the carboxylate-based zwitterions containing varying number of ether groups are highly biocompatible and mixing them with organic solvent (DMSO) enhances their biocompatibility and cellulose dissolution potential (>2 times)[38]. These results encouraged us to develop sulphonyl functionalized zwitterions with varying number of ether groups and the corresponding ILs with unconventional anions to test their cellulose dissolution capacity [39].

Scheme 1. Preparation of new *N*-oxyethylene *N*-sulfopropyl imidazolium based ionic liquids (ILs) via the corresponding sulfonate zwitterions (ZIs).



#### 2. Experimental

#### General Procedure for preparation of imidazolium based ZIs (5b, 6b, 8b, 10b).

Sodium ethoxide (2.0 eq) was dissolved in acetonitrile and stirred for 10 minutes at room temperature. Imidazole (1.0 eq) was added to the reaction mixture and stirred for additional 15 minutes (r.t.) and the appropriate alkyletherchloride 7-7" (1.0 eq) was added to the reaction mixture. The mixture was stirred for 24 hours at 80 °C and excess sodium ethoxide was filtered off. 1,3-Propanesultone 9 (1.0 eq) was added to the resulting solution of the respective *N*-oxyethyleneimidazole (**5a**, **6a**, **8a**, **10a**). The reaction mixture was heated and stirred at 80 °C for 24 hours. Solvent was removed by rotary evaporator and the respective zwitterion (ZIs **5b**, **6b**, **8b** or **10b**) was further dried at a Schlenk line for 24 hours with stirring at 50 °C.

#### General Procedure for preparation of imidazolium based ILs (5c-f, 6c-f, 8c-f, 10c-f).

The appropriate zwitterion (**5b**, **6b**, **8b**, **10b**) (1.0 eq) was dissolved in methanol (2.0 eq), and the proper acid (2.0 eq) was added to the mixture. The mixture was stirred at room temperature for 6-24 hours. Solvent and excess acid were removed under reduced pressure and the corresponding IL (**5c-f**, **6c-f**, **8c-f**, **10c-f**) was further dried on a Schlenk line for minimum 24 hours with stirring at 50 °C and by subsequent freeze drying for 24 hours.

#### Cellulose dissolution and regeneration

Cellulose dissolution was performed with all synthesized ILs (**5c-f, 6c-f, 8c-f, 10-f**). Microcrystalline cellulose (MCC, 2 wt-% of actual IL) was added to a solution of the appropriate IL (0.5 g) and dry DMF (0.5 g) at  $100^{\circ}$ C. When the actual amount of MCC was dissolved, additional small amounts (1-2 wt-% of IL at a time) was added step-wise until the IL/DMF mixture was no longer able to dissolve additional amount MCC. When dissolution of MCC was regenerated by addition of distilled water to the mixture. The mixture was stirred for 12-24 hours and the MCC was filtered off, dried and collected for further studies.

#### 3. Results and Discussion

#### 3.1. Preparation of new ILs via imidazolium sulfonate ZIs

The dual functionalized imidazolium ZIs were synthesized and used as precursors for a variety of new ILs (Scheme 1). New sulfone-based ILs (5c-f, 6c-f, 8c-f, 10c-f) with varied counter-anions were prepared from Noxyethylene imidazolium sulfonate ZIs (5b, 6b, 8b, 10b) by protonation. The ZIs were synthesized through a direct double *N*-alkylation procedure. The initial *N*-oxyethylene imidazoles (5a, 6a, 8a, 10a) were prepared from imidazole in acetonitrile at 80 °C with sodium ethoxide and the appropriate 1-Cl-2-alkoxyethanes (7-7"). The chloro-polyether reagents 7" and 7" were prepared from, respectively, the corresponding methoxy-alcohol [40] with  $SOCl_2$  and the chloro-alcohol [41] by MeI/NaOEt methylation. The resulting N-oxyethylene imidazole (5a, 6a, 8a, 10a) solutions were filtered and alkylated directly by 1,3-propanesultone (9) ring opening in ACN at 80 °C to give the ZIs 5b, 6b, 8b and 10b in up to 99 % over-all yield. The viscosity of the ZI products decreased from solid (5b) to gel-like (6b) into viscous liquids (8b, 10b) by increased ether chain length and number of oxygens. The ZIs were soluble in methanol and water, but insoluble in DMSO and DMF. The new ILs were prepared in quantitative yields (after freeze drying) by protonation of the ZIs. Treatment of the N-oxyethylene imidazolium sulfonate ZIs (5b, 6b, 8b, 10b) with sulfuric, phosphoric, trifluoromethanesulfonic and methanesulfonic acids in methanol afforded ILs 5c-f, 6c-f, 8c-f and 10c-f with the [HSO<sub>4</sub>], [H<sub>2</sub>PO<sub>4</sub>], [TfO] and [MsO] counterions, respectively. Treatment of ZI 5b with the weaker HOAc acid failed to give the corresponding IL with [OAc] counterion.

The novel dual functionalized ILs **5c-f**, **6c-f**, **8c-f** and **10c-f** were characterised by <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR, IR and TGA/T<sub>d</sub>. HRMS analyses in positive and negative mode confirmed the respective cation/anion IL structures. The ILs were applied in cellulose dissolution studies.

#### 3.2. Characterization of novel ILs; TGA and thermal stability

Thermal stability of a substance describes the resistance to permanent changes to its chemical or physical structure caused by heat. The TGA measurements, providing weight loss curves by increased temperature, were used to determine the thermal stability of the new ILs (Figure 2). The temperature at which 10 % of the total mass of the ILs decomposed is considered as the thermal stability ( $T_d$ ) of ILs [42]. The TGA temperature profiles are dependent on viscosity, heat transfer, heating rate, exo- and endothermic decomposition reactions, instrumentation, sample geometry and mass [43]. No general measurement conditions are used for the determination of thermal stability of ILs. Therefore, different reported thermal stability data are not necessarily comparable [44]. In the present study, TGA measurements of the new ILs were performed under inert atmosphere (under nitrogen flow) with a heating rate of 10 °C/min. Thermal stability of ILs depends on type of cation and anion, as well as modifications on cation, such as alkyl chain length or the nature of the substituents [44].

It has been shown that type of anion impacts the thermal stability of ILs more than the type of cation and modifications on cation [44]. This is observed in the present study, where the  $T_d$  values of ILs with the same anion differ less than ILs with the same cation (Table 1). In particular, the thermal stability within a series of [HSO<sub>4</sub>]<sup>-</sup> or [MsO]<sup>-</sup> anion based ILs have almost similar values, irrespective of the cation, as shown by the small  $T_d$  difference of only 5-6 °C for ILs **6c/8c/10c** (entry 2) and **6f/8f/10f** (entry 3), respectively. However, [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> based ILs (**5d/6d/8d/10d**) showed significant difference ( >60 °C) in  $T_d$  values by increasing the number of ether groups of the imidazolium cations. Some other effects of the IL cation was seen, as the  $T_d$  values indicate that the thermal stability drops going from the more stable ILs with the OMe-group (**5c-f**;  $T_d$  173 - 268 °C) to the corresponding OEt-ILs (**6c-f**;  $T_d$  164 - 239 °C). The ILs with longest polyether chain (**10c-f**, n = 3) do not follow the same trend as the other ILs, as the change in counter-anion only have a minor effect on the  $T_d$  value, ( $T_d$  182 - 194 °C). This may be caused by the wrapping effect of the long ether-chains, protecting the imidazolium cation towards nucleophilic attack by the anion, hence increasing thermal stability [44-46].

entry	Anion	IL	T <sub>d</sub>	IL	T <sub>d</sub>	IL	T <sub>d</sub>	IL	T <sub>d</sub>
1	$[TfO]^-$	5e	173	6e	164	8e	156	10e	187
2	$[HSO_4]^-$	5c	197	6c	178	8c	183	10c	183
3	[MsO] <sup>-</sup>	5f	210	6f	200	8f	200	10f	194
4	[H <sub>2</sub> PO <sub>4</sub> ]-	5d	268	6d	239	8d	256	10d	182

**Table 1:** Thermal degradation temperature (T<sub>d</sub>; °C) for ILs.<sup>a</sup>

<sup>a</sup> The thermal degradation point; the temperature giving weight loss of 10 wt-% IL.

Studies on thermal decomposition mechanism of ILs have shown that IL degradation may take place by e.g., elimination and rearrangement mechanism [47],[39],[48]. However, the main breakdown mechanism is dealkylation by loss of alkyl chain through anion nucleophilic substitution [43]. Therefore, the thermal stability of ILs correlates well with the anion nucleophilicity. ILs with e.g. the poor nucleophilic anions bis(trifluoromethylsulfonyl)imide [Tf<sub>2</sub>N]<sup>-</sup> have high thermal stability, while ILs with the strong nucleophilic anions Cl<sup>-</sup> are thermally less stable [48]. The acidity of the acids used for the present synthesis of ILs vary; TfOH (pK<sub>a</sub> = -14.0) > H<sub>2</sub>SO<sub>4</sub> (pK<sub>a</sub> = -3.0) > MsOH (pK<sub>a</sub> = -2.6) > H<sub>3</sub>PO<sub>4</sub> (pK<sub>a</sub> = 2.1). Most of the experimental TGA results is consistent with previously reported theory [48]. The weakest acid (H<sub>3</sub>PO<sub>4</sub>) give the strongest conjugated base and, hence, the [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> ILs with a poor anion nucleophile, result in the highest IL thermal stability, as seen by the TGA curves (Figure 2; **5d**, **6d**, **8d**, **10d**). In contrast, the strong acidity of TfOH explains the general low thermal stability shown by the TGA curves of the [TfO]<sup>-</sup> ILs (Figure 2; **5e**, **6e**, **8e**, **10e**). In contrast to ILs with simple alkyl group, the dual functionalized ILs in this study undergo stepwise degradation, since the sulphonyl and ether functional group may undergo thermal degradation by different mechanisms at different temperature intervals [39].

In accordance with the TGA observations, the  $T_d$  values of ILs **5c-f**, **6c-f** and **8c-f** increase in the expected anion order;  $[TfO]^- < [HSO_4]^- < [H_2PO_4]^-$  (Table 1), hence, giving increasing IL stability: **5e/6e/8e < 5c/6c/8c** < **5f/6f/8f < 5d/6d/8d**.



Figure 2: TGA curves for ILs (a) ILs 5c-f. (b) ILs 6c-f. (c) ILs 8c-f. (d) ILs 10c-f.

#### 3.3. Studies on cellulose dissolution

The dual functionalized ILs **5c-f**, **6c-f**, **8c-f** and **10c-f** were synthesized to be tested for cellulose dissolution. It is known that good cellulose solubilities (> 25 wt-%) are observed for pure ILs [49]. However, a major limitation of ILs is their high viscosity, which hinder the cellulose dissolution and many post processes such as electrospinning. This issue can be overcome by the addition of aprotic organic solvents (DMSO, DMF, etc), which will decrease the viscosity without the precipitation of cellulose [31]. Moreover, the addition of solvents can drastically reduce the cellulose dissolution time ( $\approx$  2 order of magnitude) compared to the pure ILs [50]. In addition, ILs-solvent system can dissolve high concentration of cellulose (>15 wt-%), even at ambient conditions [51]. By taking all these factors under consideration, the dissolution experiments were carried out in DMF/ILs solutions. The cellulose dissolution is a 1:1 mixture of IL (0.5 g) and dry DMF (0.5 g) at 100 °C (Table 2). The dissolutions were performed by step-wise addition-dissolution of small amounts of MCC (1-2 wt-% MCC of IL at the time) until the MCC-IL/DMF solutions were saturated. The dissolution efficiencies were measured relative to amount of IL used (wt-% MCC of IL).

entry	ILs	IL cation	IL anion	Solubility	β	time
			C	(wt-% of IL)	(H-bond	(h)
					basicity)	
1	5c	O C	[HSO <sub>4</sub> ]	15.1	0.60	72
2	5d		[H <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	16.1	1.10	72
3	5e	ОН	[TfO] <sup>-</sup>	16.4	0.37	72
4	5f		[MsO] <sup>-</sup>	15.4	0.82	72
5	6c		[HSO <sub>4</sub> ]	19.8	0.63	72
6	6d		[H <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	19.6	1.11	72
7	6e	ОН	[TfO] <sup>-</sup>	18.8	0.40	72
8	6f		[MsO]	18.5	0.84	72
9	8c		[HSO <sub>4</sub> ]	10.9	0.75	48 <sup>b</sup>
10	8d		[H <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	9.7	1.24	48 <sup>b</sup>
11	8e	ÓH	[TfO] <sup>-</sup>	14.5	0.42	96
12	8f		[MsO] <sup>-</sup>	13.9	0.98	96
13	10c		[HSO <sub>4</sub> ]	9.0	0.73	24 <sup>b</sup>
14	10d		[H <sub>2</sub> PO <sub>4</sub> ] <sup>-</sup>	8.2	1.17	24 <sup>b</sup>
15	10e	ОН	[TfO] <sup>-</sup>	12.7	0.50	48 <sup>b</sup>
16	10f		[MsO]	13.4	0.92	48 <sup>b</sup>

**Table 2:** MCC cellulose dissolution in Ils.<sup>a</sup>

<sup>a</sup> Dissolution conditions; 1:1 ratio of IL / dry DMF (0.5 g + 0.5 g), 100  $^{\circ}$ C. Results are given in wt-% MCC dissolved in weight of IL. <sup>b</sup> The experiment was stopped after 24/48 hours, due to saturation of IL/DMF solution.

The results show that more than double dissolution capacity was obtained going from tri-ether IL **10c** to monoether **6c**, (entries 13,5). The *N*-oxyethylene-ILs with the less number of electronegative ether oxygens (n = 1), such as the MeO-ILs **5c-f** (entries 1-4, 15.1-16.4 wt-% of IL) and, particularly, the EtO-ILs **6c-f** (entries 5-8, 18.9-19.8 wt-% of IL), had highest dissolution potential. Maximum cellulose dissolution capacity, up to 20 wt-% (of IL), was obtained with the EtO-ethyl-imidazolium based IL with the  $[HSO_4]^-$  counter-ion (**6c**, entry 5). The highest MCC dissolution efficiency of the EtO-ILs may be explained by the larger electron donating effect of the ethoxy (EtO) group compared to the methoxy (MeO) group. The activation of the EtO-ILs enables more effective interaction with the cellulose H-bond network and increases the dissolution potential. Longer imidazolium cation ether chains (n = 2 or 3) reduce the dissolution abilities of the ILs, as seen from the moderate cellulose dissolution obtained in ILs **8c-f** (entry 9-12, 9.7-14.0 wt-% of IL) and **10c-f** (entry 13-16, 8.2-13.4 wt-% of IL). This is in agreement with previous studies on cellulose dissolution in tetraalkyl-phosphonium ILs, reporting that tetrabutylphosphonium ILs were not able to dissolve cellulose even at > 130 °C because of the bulky nature of the ILs [52].

The  $pK_a$  of the anions of ILs did not have a systematic influence on the ILs cellulose dissolution capability. In average, as ILs with the weakest base, TfO<sup>-</sup> (**5e**, **6e**, **8e**, **10e**, entries 3,7,11), performed best. However, H-bond Submitted to *Journal of Molecular Liquids* 6

basicity of ILs is considered as one of the most important parameters to determine IL cellulose dissolution potential by cleavage of inter-/intramolecular hydrogen-bonds. The electron donating ability of a solvent to form hydrogen bonds with protons of a solute is given by the  $\beta$  value, also called the Hydrogen Bond Accepting (HBA) basicity. In general, the IL cellulose dissolution potential increases by increased  $\beta$  value [53]. Because of the experimental difficulties associated with the measurement of  $\beta$  value of the synthesized ILs (high viscosity and water sensitivity), the  $\beta$  values are calculated using a theoretical model. In addition, our research group is in the process of developing a fast and reliable machine learning model to predict the Kamlet-Taft parameters of ILs. An earlier model reported by Cláudio *et al.* [54] for predicting  $\beta$ , was extended to include more structurally diverse cations and anions (see Supporting Information). The model was used to estimate the  $\beta$  values for the ILs investigated in this study (Table 2).

Limited studies on ILs with the unconventional anions applied in the present work is known. In our series of IL ion pairs, varying the cation had greater impact on MCC cellulose dissolution ability, than the minor effect obtained by anion exchange. The dissolution capacity of the most efficient ILs, 5 and 6 with MeO- or EtOethylimidazolium cations (Table 2, entries 1-8), mainly follow the H-bond basicity trend, as their  $\beta$  values (0.4-1.1) correlate with the corresponding cellulose dissolution ability (15.1-19.8 wt-%). However, the IL cellulose dissolution capacity does not always correlate with the H-bond basicity. For instance, the [H<sub>2</sub>PO<sub>4</sub>] anion based ILs have significantly higher  $\beta$  value (Table 2, entries 2,6,10,14) than the other ILs, while the dissolution capacity of e.g. the  $[H_2PO_4]$  anion mono-ethers ILs 5d, 6d (entries 2,6) was almost comparable to the other anion mono-ether ILs. This is probably due to the lower acidity of [H<sub>2</sub>PO<sub>4</sub>] based ILs with a sulphonyl group (-SO<sub>3</sub>H) on the cation [37], affording weaker cellulose interaction of the cation and lower cellulose dissolution potential. Even more, the combination of the general shielding effect of the bulky polyether groups and the low acidity of the [H<sub>2</sub>PO<sub>4</sub>] based SO<sub>3</sub>H-ILs may explain the minimum dissolution (<10 wt-%) for polyether ILs 8d and 10d (n=2,3; entries 10,14), despite having the highest  $\beta$  value (approx. 1.2). The group of [OTf] based ILs (5e, 6e, 8e, 10e) with the lowest  $\beta$ values (0.37-0.5; entries 3,7,11,15), also represents an exception, having among the highest dissolution abilities (12.7-18.8 wt-%). This discrepancy may be explained by dissociation of [OTf] based ILs in DMF solvents. It is known that addition of oxygen containing organic solvents to imidazolium based [OTf] ILs affords IL dissociation, and consequently, formation of free [OTf] anions [55, 56]. The presence of free [OTf] anions in the IL/DMF systems may increase the interaction with H-bonds in cellulose and would explain the more efficient cellulose dissolution in [OTf] based ILs.

In summary, the present study on cellulose dissolution ability of dual functionalized (poly-)ether sulphonate ILs demonstrates that the polyether chain length of the IL cation plays a more important role than the anion character, in contrast to previous observations for conventional ILs [19]. The IL dissolution ability increases going from ILs with longer imidazolium cation ether chains (n = 2 or 3) to corresponding mono-ether ILs (n=1).

After complete MCC dissolution, the cellulose samples were regenerated by addition of water, filtered and dried for further XRD and TGA studies. TGA curves of the pure MCC and the regenerated MCC after treatment with **5c-5f** are shown in Figure 4. TGA analysis confirmed changes in the thermal stability of MCC cellulose after IL dissolution. The graphs show a lower onset temperature for regenerated MCC (240 °C) than pure untreated MCC (280 °C), which is in accordance with literature [57]. All the TGA curves show continuous decompositions, and not stepwise as seen from the IL curves (Figure 2).

<sup>1</sup>H NMR of all ILs before and after cellulose dissolution showed that no change in the IL structures had taken place, proving that ILs can perform cellulose dissolution at 100 °C without IL decomposition.



Figure 4. TGA of original MCC and regenerated cellulose after dissolution in ILs 5c-f.

X-ray diffraction (XRD) analysis was used to study the structural changes taking place by cellulose dissolution and regeneration. XRD pattern of the original and regenerated MCC after dissolution in the most promising ILs, **5c-f, 6c-f**, were recorded (Figure 5a and 5b). In general, XRD of native cellulose samples exhibit typical cellulose diffraction peaks, where the highest peak corresponds to the 002 crystallographic planes. The intensity of the 002 peak in MCC gives information on the extent of crystallinity. When cellulose dissolves in ILs by cleavage of the inter- and intramolecular hydrogen bonds between the poly-glucose layers, the crystallinity decreases and MCC transforms from cellulose I to cellulose II [58]. However, the presence of cellulose I has also been observed after complete dissolution of cellulose in ILs [59-62], as the crystalline cellulose I may partially transform into a lower crystalline structure, giving XRD patterns with lower peak intensities. In accordance to these reports, our study show that all the crystallographic diffraction peaks are significantly reduced after MCC dissolution and regeneration (Figure 5). The results suggest that the regenerated samples contain a less ordered cellulose crystalline structure than the original MCC.



Figure 5: XRD of original MCC and regenerated cellulose after dissolution in ILs a) 5c-f and b) 6c-f.

#### 4. Conclusion

The synthesis of new dual functionalized imidazolium based ILs with (poly-)ether (n = 1-3) and sulphonic acid functional groups is reported. The ILs based on *N*-oxyethylene-*N*-sulfopropylimidazolium cations were prepared via the respective *N*-oxyethylene imidazolium sulfonate zwitterions ions (ZIs, 74-99%) by double *N*-imidazole alkylation, including 1,3-propanesultone ring opening. ZI protonation with the appropriate acid allowed incorporation of the less frequently used [HSO<sub>4</sub>]<sup>-</sup>, [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup>, [TfO]<sup>-</sup> and [MsO]<sup>-</sup> counter-ions in the new ILs. Characterization by TGA analysis revealed that the novel ILs are stable up to 210 °C.

The capacity of the new ILs to dissolve MCC cellulose in solutions of ILs and DMF was studied. In general, the nature of the polyether chain length of the IL cations had higher impact (n=1 > n=2,3) on the cellulose dissolution ability than the IL anion. Results showed that high MCC dissolution efficiency (15-20 wt-% of IL) was observed in 1:1 DMF/ILs solutions at 100°C in 72 hours by applying the MeO-/EtO-monoethyl-imidazolium based ILs with any of the counter-ions. In particular, the highest cellulose dissolution potential, up to 20 wt-% (of IL), was obtained with the EtO-ethyl-imidazolium based IL with the [HSO<sub>4</sub>]<sup>-</sup> counter-ion. Hydrogen bond basicity ( $\beta$ ) of the synthesized ILs were predicted using DFT calculations. The original MCC and the regenerated cellulose samples were characterized by XRD and TGA analysis.

This study demonstrates the new opportunities provided by organic synthetic approaches for development of tailor made unconventional ILs for cellulose dissolution. The work emphasises the potential of ILs derived from zwitterions and the corresponding mixtures with aprotic organic solvent for cellulose processing. The results clearly show that modification on the cationic core may contribute significantly to the cellulose dissolution potential of ILs.

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#### **Supporting Information**

Supplementary material related to this article (synthesis and characterization of ZIs and ILs; copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of ZIs and ILs and theoretical model for predicting IL  $\beta$  values) can be found in the on-line version at doi: .....

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Graphical abstract

### Highlights

- Synthesis of new dual functionalized ionic liquids (IL) with unconventional anions
- Cellulose dissolution of the oxyethylene-sulfopropyl imidazolium ILs was studied
- New ILs dissolved up to 20 wt% cellulose (MCC, DMF/ILs, 100°C)
- Shorter IL polyether chain length increased (1 >2,3) dissolution ability
- IL cations (polyether chain length) affect dissolution ability more than IL anions

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