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Article

# Evaluating the Hydrothermal Stability of Superbase–Based Ionic Liquids in Cellulose Fiber Spinning

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enium  $[mTBDH]^+$  in  $[mTBDH][MeOCH_2COO]$  compared to [mTBDH][OAc], as well as the strong cellulose dissolution capability of  $[mTBDH][MeOCH_2COO]$  and excellent spinnability with a maximum draw ratio of 14. These findings demonstrate the high potential of using  $[mTBDH][MeOCH_2COO]$  as the solvent to advance Ioncell fiber spinning technology by reducing the hydrolysis rate of  $[mTBDH]^+$ , thereby minimizing loss during solvent recycling processes.



# **INTRODUCTION**

Ionic liquids (ILs) are emerging as promising substitutes for traditional solvents in the dissolution of biopolymers, facilitating the production of regenerated fibers.<sup>1,2</sup> This is attributed to their low volatility, high dissolution capability, chemically inertness and environmentally friendly characteristics.<sup>3,4</sup> ILs that are capable of dissolving cellulose typically include anions exhibiting strong hydrogen bond basicity, such as chloride, carboxylates, and phosphates.<sup>5-7</sup> The anions form hydrogen bonds with cellulose hydroxyl groups, while the bulky cations assist in the separation of negatively charged constituents.<sup>8,9</sup> Alkylated imidazole or super bases are commonly employed as cations in ILs designed for cellulose dissolution.<sup>10–13</sup> For instance, BASF utilized [emim][OAc] as a solvent in the production of cellulosic fibers.<sup>14</sup> However, during dissolution, spinning, and IL recycling, the C2 carbon of the imidazolium ring reacts with cellulose, resulting in an imidazolium adduct, and trans-acylation reactions can modify the cellulosic solute.<sup>15–17</sup> Superbase–based ILs, such as 1,5diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (mTBD), have shown particular potential for their ability to dissolve cellulose and other natural polymers and spin them into fibers with desirable mechanical properties.<sup>12,18,19</sup> This has led to the development of the Ioncell process, which uses superbase-based ILs to convert cellulose resources such as pulp, paperboard, and cotton into highperformance textile fibers.<sup>20,21</sup> Compared with imidazoliumbased ILs, superbase-based ILs are inert toward cellulose and cause less degradation of cellulose.<sup>6</sup>

The first superbase-based IL used in Ioncell was [DBNH]-[OAc], which showed excellent spinnability and was highly tolerant to various cellulose raw materials and additives.<sup>22,23</sup> However, during the distillation recycling of [DBNH][OAc], a significant amount of hydrolysis products was formed (14.4 wt %), leading to reduced dissolution capacity toward cellulose.<sup>24</sup> To overcome this limitation, a guanidine-based IL with improved thermal stability, [mTBDH][OAc], was introduced and used as cellulose solvent in the Ioncell process. It demonstrated significantly higher thermal and hydrolytic stability during solvent recovery, producing only 1.6 wt % hydrolysis products in five cycles.<sup>25</sup>

Additionally, mTBD is a stronger superbase than DBN ( $pK_a = 25.4$  and 23.4, respectively, measured in acetonitrile solvent),<sup>26,27</sup> exhibiting higher proton affinity and resulting in a lower vaporization rate of mTBD during thermal recycling. Consequently, the recovered [mTBDH][OAc] has an acid/ base (A/B) ratio of 1.1, while the A/B ratio of recovered [DBNH][OAc] is 1.3, reducing its dissolution capacity for cellulose and changing the rheological properties of the resulting solution.<sup>24</sup> The higher hydrothermal stability and tolerance to alterations are clear advantages of mTBD, making it an excellent candidate for further development of this solvent in the Ioncell process. However, [mTBDH][OAc] has a high melting temperature of 78 °C (Figure S1), causing processing challenges and high energy consumption. Our recent study reveals that substituting acetic acid with levulinic acid in

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[mTBDH][OAc] resulted in the production of a room temperature IL, [mTBDH][Lev], demonstrating remarkable dissolution capacity toward both cellulose and wool.<sup>2</sup> Additionally, Li et al. conducted a study wherein they synthesized DBN- and DBU-based ILs combined with various anions, and focusing on characterizing melting temperature, cellulose solubility, and the resulting mechanical properties of regenerated cellulose films.<sup>29</sup> Among these, methoxyacetate looks promising, forming a room temperature IL in conjugation with DBU and DBN. The [DBNH]-[MeOCH<sub>2</sub>COO] and [DBUH][MeOCH<sub>2</sub>COO] can dissolve 14.6 and 16 wt % of cellulose respectively with a DP of 156 at 80 °C.<sup>29</sup> These cellulose solutions have been successfully processed into regenerated cellulose films. Nevertheless, the preceding studies did not explore the impact of anions on the thermal stability of the conjugated super bases. In this work, we investigated the thermal stability and hydrolysis kinetics of [mTBDH][MeOCH<sub>2</sub>COO] aqueous solution, as well as its application in regenerated cellulose fiber spinning. Our hypothesis is that acids with stronger acidity can stabilize the structure of super bases, leading to a reduction in the hydrolysis rate. MeOCH<sub>2</sub>COOH has a  $pK_a$  of 3.53, while acetic acid has a  $pK_a$  of 4.76. We specifically chose to use 10 wt % water because our previous study revealed that the highest hydrolysis rates for [mTBDH][OAc] occurred in the presence of 10-20 wt % water.<sup>30</sup>

## MATERIALS AND METHODS

**lonic Liquid Preparation.** [mTBDH][MeOCH<sub>2</sub>COO] was prepared by neutralization of mTBD with an equimolar amount of methoxyacetic acid (98%, Merck, Germany) at room temperature (23 °C) under stirring. Because the neutralization process is exothermic, the methoxyacetic acid was added slowly to the mTBD to avoid overheating. The mixture was subsequently stirred for another 30 min to ensure complete conversion. Since [mTBDH][MeOCH<sub>2</sub>COO] is a liquid at room temperature, heating is not required for its preparation.

**NMR Analysis.** The hydrolysis reactions of [mTBDH]-[MeOCH<sub>2</sub>COO] were carried out under an inert atmosphere of argon by the standard Schlenk technique. The samples were measured using <sup>1</sup>H NMR spectrometry (Bruker Avance III 400) and analyzed using MestReNova software. DMSO- $d_6$  was used as the solvent for NMR analysis.

**Dope Preparation.** Dissolution of cellulose pulp (spruce acid sulphite pulp) in ionic liquid [mTBDH][MeOCH<sub>2</sub>COO] was performed in a small vertical kneader at 85 °C under 10–20 mbar vacuum for 2 h. The dissolution process was monitored using polarized optical microscopy. After 2 h, a preheated hydraulic press filtration system with a 5–6  $\mu$ m mesh metal filter fleece was used to remove the undissolved cellulose fibers at 85 °C and 150–200 bar. The chemical composition and molar mass of the cellulose pulp listed in Table 1 were analyzed using a standardized protocol consistent with previously published methods.<sup>31</sup>

**Rheology Measurement.** The viscoelastic properties of cellulose dopes under shear stresses were measured using an Anton Paar MCR 302 rheometer equipped with 25 mm diameter parallel plate geometry and 1 mm gap size. The viscoelastic behavior was studied by conducting dynamic frequency sweeps at various temperatures ranging from 50 to 90 °C, within an angular frequency range of  $0.01-100 \text{ s}^{-1}$  and a strain of 1%. The zero-shear viscosity,  $\eta^{\circ}$ , was determined by

 Table 1. Chemical Composition and Molar Mass of the

 Cellulose Pulp

cellulose	95.1% on pulp
hemicellulose	4.6% on pulp
lignin	
ash	0.07% on pulp
intrinsic viscosity	571 mL/g
Mn	56,000 Da
Mw	198,000 Da
Mz	414,000 Da
PDI	3.5
DP > 2000	20.0%
DP < 100	5.5%

fitting the complex viscosity data to the Cross viscosity model, assuming that the Cox-Mertz rule is valid. The master curves of spinning dopes at their spinning temperature were generated based on the time temperature superposition principle.

**Monofilament Fiber Spinning.** A small amount of dope (approximately 20 g) was placed into a monofilament dry-jet wet spinning unit (manufactured by Fourné Polymertechnik) and heated to its spinning temperature (85-95 °C), determined by its rheological properties. Then the dope was extruded through a capillary with a diameter of 100  $\mu$ m and length of 200  $\mu$ m into an air gap where the dope was stretched to reach different draw ratios (DRs) before regeneration in water coagulation bath. The water bath was kept at 5-6 °C. The extrusion velocity was kept constant at 1.3 m/min, while the take-up velocity (the speed of the godets collecting the fibers) was varied to collect fibers at different DRs. The collected filaments were cut into 8 cm long pieces and washed with 80 °C water for 2 h to remove any residual IL.

**Tensile Testing.** The mechanical properties of the cellulose fibers in the conditioned and wet state were determined by using a Favigraph automatic single-fiber tester (Textechno H. Stein GmbH & Cpo, Germany) based on the ISO 5079 standard (20 mm gauge length, 0.06 cN/tex pretension, 20 mm/min test speed). All of the fibers were conditioned overnight ( $20 \pm 2 \degree C$ ,  $65 \pm 2\%$  relative humidity) before the testing. Twenty fibers from each sample were tested at 20  $\degree C$  and 65% RH.

# RESULTS AND DISCUSSIONS

The hydrolysis test of ILs at elevated temperatures (95  $^{\circ}$ C) was conducted under an inert atmosphere of argon, and the compositional changes over time were monitored using <sup>1</sup>H NMR (Figure 1 and Table S1).

The bicyclic guanidine-based IL [mTBDH][OAc] exhibits a central CN3 core composed of an "R–C(==NH)–NH<sub>2</sub>" amidine moiety and a tertiary nitrogen. In the presence of acids, it undergoes protonation, forming a rigid covalent N–H bond that stabilizes its structure. Water promotes ring opening at elevated temperatures, resulting in the formation of cyclic urea.<sup>30,32</sup> The CH<sub>3</sub> groups in all structures, including mTBD, MeOCH<sub>2</sub>COOH, and H-mTBD, induce strong NMR signals illustrated as a singlet, making it easily distinguishable by the distinct chemical shifts. In [mTBDH]<sup>+</sup>, the CH<sub>3</sub> group protons are illustrated as a singlet at 2.98 ppm (Figure 1). The ring opening causes a shift of the –CH<sub>3</sub> signal to 2.37 and 2.76 ppm in [1-H-mTBDH]<sup>+</sup> and [2-H-mTBDH]<sup>+</sup>, respectively.

In  $[mTBDH][MeOCH_2COO]$ ,  $[mTBDH]^+$  degrades rapidly within the first 24 h, then gradually tapers off and reaches a



Figure 1. [mTBDH][MeOCH<sub>2</sub>COO] (A/B 1:1, 10 wt % water, 95 °C) hydrolysis as a function of time analyzed using <sup>1</sup>H NMR spectroscopy in dimethyl sulfoxide (DMSO)- $d_{6}$ .

Table 2. Kinetic Parameters of the Degradation of  $[mTBD]^+$ in the Ionic Liquid  $[mTBDH][MeOCH_2COO]$  in Comparison to  $[mTBDH][OAc]^{30}$  at 95 °C and in the Presence of 10 wt % Water

parameter	unit	[mTBDH][OAc]	[mTBDH] [MeOCH <sub>2</sub> COO]
$[mTBD]_0$	mole %	$48.3 \pm 0.5$	$46.7 \pm 0.5$
$k_1$	$h^{-1}$	$0.0037 \pm 0.0002$	$0.00056 \pm 0.0000932$
$k_2$	$h^{-1}$	$0.00093 \pm 0.0001$	$0.0018 \pm 0.000364$
$[mTBD]_{\infty}$	mole %	9.7	35.53
$K_{\rm c}$		4.0	0.31

plateau. After 24 days of incubation, the hydrolysis product  $[H-mTBD]^+$  reached its maximum amount, 5.5 mol %, as determined by the integration of peaks at 2.75 and 2.23 ppm (Table S1). However, the amount of  $[mTBDH]^+$  continuously decreased and eventually stabilized at approximately 40 mol % after 2 months of incubation. Despite using argon protection, some evaporation still occurred over the two months. We noticed a thin layer of liquid condensate in the chilled areas



Figure 2. Degradation of mTBD in the ionic liquid [mTBDH]-[MeOCH<sub>2</sub>COO] in comparison to [mTBDH][OAc]<sup>30</sup> at 95 °C and in the presence of 10 wt % water.

above the reaction flask. NMR analysis of this condensate showed higher concentrations of  $[H-mTBD]^+$  and  $[MeOCH_2COO]^-$  at 11.4 and 66 mol %, respectively. In our

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Figure 3. Rheological properties of 13 wt % cellulose dopes. (a) Master curve of  $[mTBDH][MeOCH_2COO]$  dopes (black symbols) and [mTBDH][OAc] (blue symbols) at 90 °C. Square, sphere and circle symbols represent complex viscosity, G' and G" respectively. (b) Zero shear viscosity and COP angular frequency calculated as a function of temperature. Square symbols denote zero shear viscosity and sphere symbols represent COP angular frequency.



Figure 4. Mechanical properties of regenerated cellulose fibers (average of 20 individual tests). (a)  $[mTBDH][MeOCH_2COO]$  as the solvent (b) [mTBDH][OAc] as the solvent. The stress-strain curves were measured at 65% RH and 20 °C.

previous distillation study of [mTBDH][OAc], we found that mTBD has a higher vapor pressure than its hydrolysis products and acetic acid. As a result, the evaporated acid likely condensed in the chilled region while mTBD evaporated. Moreover, there was a shift in the CH<sub>2</sub> protons of  $[MeOCH_2COO]^-$  from 3.47 to 3.58 ppm, indicating increased acidity in the solution, particularly after 44 days.

To understand and predict the hydrolysis reaction of  $[mTBDH][MeOCH_2COO]$ , we applied a reverse first-order kinetics model to fit our data. To simplify the modeling, we grouped the byproducts together as one entity in our model as  $[\sum mTBD_{deg}]$ 

$$[mTBD] + H_2O \rightleftharpoons \left[\sum H - mTBD + \sum A - mTBD\right]$$
$$= \left[\sum mTBD_{deg}\right]$$
(1)

Forward  $(k_1)$  and backward  $(k_2)$  reactions are both pseudo first-order. Thus, the concentration of mTBD after time t,  $[mTBD]_t$  can be calculated by eq 2

$$[mTBD]_{t} = [mTBD]_{0} \left\{ \frac{k_{2} + k_{1} e^{-(k_{1} + k_{2})t}}{k_{1} + k_{2}} \right\}$$
(2)

The equilibrium concentration of mTBD,  $[mTBD]_{\infty}$ , is estimated by eq 3

$$[mTBD]_{\infty} = \frac{k_2 [mTBD]_0}{(k_1 + k_2)}$$
(3)

and the equilibrium constant  $K_c = d[mTBD]/dt = 0 \rightarrow k_1[mTBD] = k_2[\sum_m TBD_{deg}]$  with eq 4

$$K_{\rm c} = \frac{\left[\sum {\rm mTBD}_{\rm deg}\right]}{\left[{\rm mTBD}\right]_{\infty}} = \frac{k_1}{k_2} \tag{4}$$

In our investigation into the influence of anions on the hydrolysis reaction of  $[mTBDH]^+$  in the corresponding ionic liquid, we conducted a comparative analysis of the kinetic coefficients of  $[mTBDH]^+$  degradation, as presented in Table 2. The forward hydrolysis rate of mTBD in [mTBDH][OAc] ( $k_1 = 0.0037$ ) significantly surpasses that in [mTBDH]-[MeOCH<sub>2</sub>COO] ( $k_1 = 0.00056$ ), indicating a notably faster hydrolysis rate in the presence of acetic acid. The higher equilibrium constant  $k_c$  observed in [mTBDH][OAc] suggests a greater preference for the formation of hydrolysis products [ $\sum mTBD_{deg}$ ] when utilizing acetic acid as the anion. This observation supports our hypothesis that anions with stronger acidity can stabilize the super base structure, consequently reducing its hydrolysis rate.

The stability of the superbase mTBD was significantly enhanced when it was conjugated with methoxyacetic acid compared to acetic acid, as demonstrated in Figure 2. Thermogravimetric analysis (TGA) reveals that [mTBDH]-[MeOCH<sub>2</sub>COO] decomposes at a slightly higher temperature than [mTBDH][OAc], with derivative peak temperatures at 275 and 250 °C (Figure S1). Subsequently, we explored the capability of [mTBDH][MeOCH<sub>2</sub>COO] to dissolve cellulose and examined its spinnability. We successfully prepared a 13 wt % cellulose dope and characterized its rheological properties, comparing them to those of a [mTBDH][OAc] dope, as presented in Figure 3. Based on our previous study, the viscoelastic properties of cellulose dissolution in ionic liquids, especially the crossover point (COP), where the storage modulus (G') intersects with the loss modulus (G'') and zero shear viscosity ( $\eta^{0*}$ ), are important parameters to evaluate spinnability.<sup>33</sup> G' and G'' indicate the elastic and viscous behavior of the dope, respectively. The COP represents the frequency at which the solution's elastic and viscous behaviors are equivalent. The determination of  $\eta^{0*}$  involved fitting the Cross model to the complex viscosity curve, assuming validity of the Cox–Merz rule.<sup>34</sup>

In Figure 3a, we present the master curves of G', G'' and dynamic viscosity as a function of angular frequency, derived from small amplitude oscillation shear tests with 13 wt % cellulose solution. At low frequencies, the viscous nature of the cellulose solution prevails, as indicated by the higher G'' value compared to G'. As the frequency increases, the elastic property becomes more dominant. This transition arises from the greater mobility of cellulose molecules at low frequencies due to the relatively slow deformation. However, at high frequencies, the entanglement points among cellulose chains act as fixed joints, hindering the flowability of molecules. The COP angular frequency of the [mTBDH][MeOCH<sub>2</sub>COO] dope is lower than that of the [mTBDH][OAc] dope, indicating a higher degree of elastic behavior of the [mTBDH][MeOCH<sub>2</sub>COO] dope. The  $\eta^{0*}$  of the [mTBDH]-[MeOCH<sub>2</sub>COO] dope was slightly higher than that of [mTBDH][OAc], necessitating a higher shear force to induce flow. Furthermore, the [mTBDH][MeOCH<sub>2</sub>COO] dope demonstrated good spinnability with a maximum draw ratio (DR) of 14, and the mechanical properties of the resulting fibers were compared with fibers spun from [mTBDH][OAc] dope. Their mechanical properties are in the same range, with an ultimate strength of approximately 50 cN/tex and breaking strain of 6-8% (Figure 4 and Table S2).

# CONCLUSIONS

Our study demonstrates a substantial reduction in  $[mTBDH]^+$ degradation by substituting the acetate anion with methoxyacetate in the IL, evident from the higher equilibrium concentration of  $[mTBDH]^+$  (35.5 mol %) in  $[mTBDH]_ [MeOCH_2COO]$  compared to 9.7 mol % in [mTBDH][OAc]. Given its excellent spinnability,  $[mTBDH][MeOCH_2COO]$ exhibits promising potential as a solvent for large-scale regenerated cellulose fiber production. Future investigations will focus on multifilament fiber spinning, the recyclability of  $[mTBDH][MeOCH_2COO]$ , and the conjugation of methoxyacetic acid with other superbases, such as DBN and DBU, to evaluate their impact on hydrolysis reduction.

# ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c04081.

NMR raw data of [mTBDH][MeOCH<sub>2</sub>COO] at 95 °C with 10 wt % water (Table S1); tensile testing results of fibers at different draw ratios using [mTBDH]-[MeOCH<sub>2</sub>COO] and [mTBDH][OAc] as the solvent (Table S2); thermal properties of [mTBDH]-

[MeOCH<sub>2</sub>COO] and [mTBDH][OAc] (Figure S1) (PDF)

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### Notes

The authors declare no competing financial interest.

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