



## Recyclable deep eutectic solvent for the production of cationic nanocelluloses



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### ABSTRACT

Deep eutectic solvents (DESs) are potential green systems that can be used as reagents, extraction agents and reaction media. DESs are often biodegradable, easy to prepare and have low toxicity. In this work, a recyclable DES formed from aminoguanidine hydrochloride and glycerol (AhG) was used as a reaction medium and reagent (aminoguanidine hydrochloride) for the production of cationic nanocelluloses. Under mild conditions (i.e., a reaction time of 10 min at 70 °C), dialdehyde celluloses (DACs) with two different aldehyde contents (2.18 and 3.79 mmol g<sup>-1</sup>) were cationized by AhG DES to form cationic dialdehyde celluloses (CDACs). Both CDACs achieved a similar high charge density of approximately 1.1 mmol g<sup>-1</sup>. At 80 °C (for 10 min), a very high cationic charge density of 2.48 mmol g<sup>-1</sup> was obtained. The recyclability of AhG DES was demonstrated by reusing it five times without decreasing the reaction efficiency. In particular, due to the low consumption of aminoguanidine hydrochloride, high recycling efficiency could be achieved without the use of any additional chemicals. The cationized celluloses, CDACs, were further mechanically disintegrated to obtain cationic nanocelluloses. According to the initial aldehyde content of DACs, the morphology of the nanocellulose could be tailored to produce highly cationic cellulose nanofibrils (CNFs) or cellulose nanocrystals (CNCs). Transmission electron microscopy confirmed that individual CNFs and CNCs with an average width of 4.6 ± 1.1 nm and 5.7 ± 1.3 nm, respectively, were obtained. Thus, the results presented here indicate that the AhG DES is a promising green and recyclable way of producing cationized CNFs and CNCs.

### 1. Introduction

Selection of the appropriate reaction medium is critical to many chemical processes, and c.a. 80% of all consumed chemicals are used as solvents for different purposes (Cruz, Jordão, & Branco, 2017). Traditional solvents are usually prepared from non-renewable and toxic petrochemical derivatives (Gu & Jérôme, 2010), and they are often highly volatile, flammable and problematic for the environment. (Alonso et al., 2016) As a consequence of the depletion of oil resources and increasing environmental awareness, there has been growing interest in exploring alternative solvents such as water, (Li & Chen, 2006) fluorinated compounds, (Khaksar, 2015) and ionic liquids (ILs) (Imperato, König, & Chiappe, 2007) in the past decade. Although promising results have been reported, obvious limitations (such as high cost and requirement for high purity of ILs) still restrict their practical use in many cases. Therefore, new green and easily available solvents are in high demand (Zhang, De Oliveira Vigier, Royer, & Jérôme, 2012).

Currently, deep eutectic solvents (DESs) are of particular interest. The complexation of a hydrogen bond acceptor (HBA, which is typically a halide salt of quaternary ammonium) with a hydrogen bond donor (HBD, e.g., urea and glycerol) results in the formation of an eutectic mixture with a relatively low melting point, and this is how DESs are usually produced (Paiva et al., 2014; Sirviö, Visanko, & Liimatainen, 2015; Smith, Abbott, & Ryder, 2014; Wagle, Zhao, & Baker, 2014; Zhang et al., 2012). DES candidates are abundant, and they can be produced from inexpensive, biodegradable and recyclable ingredients (Ilgen et al., 2009; Singh, Lobo, & Shankarling, 2011; Sirviö, Visanko, Ukkola, & Liimatainen, 2018). Similar to ILs, DESs exhibit good solvent capacity and have a low vapor pressure that limits VOC emissions (Sirviö, Visanko et al., 2015; Sirviö, Visanko, & Liimatainen, 2016; Smith et al., 2014). However, it is much easier to prepare DESs (by straightforward mixing and heating), and they are less sensitive to impurities and usually cheaper to prepare than ILs (Wang et al., 2016). These unique properties make DESs promising green solvents and

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chemicals for sustainable biomaterial production processes.

Cellulose is known as the most abundant natural biopolymer on earth. In addition, renewability, biodegradability, and low toxicity are all inherent green characteristics of cellulose (Credou & Berthelot, 2014; Schenzel, Hufendiek, Barner-Kowollik, & Meier, 2014). Nanocelluloses, which are described as nano-structured celluloses and are often referred to as elongated cellulose nanofibrils (CNFs) or rigid cellulose nanocrystals (CNCs), have been considered as future biomaterials in recent years (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Depending on the raw materials and production methods, CNFs are mostly 3–100 nm in width and several micrometers in length (Klemm et al., 2011), whereas CNCs have a similar diameter but are shorter and have a more rod-like crystalline structure. Nanocelluloses possess certain inherent chemical characteristics (e.g., three reactive hydroxyl groups in each repeating unit) of celluloses, are lightweight (Mohieldin, Zainudin, Paridah, & Ainun, 2011), and have high mechanical strength (Oksman, Mathew, Bondeson, & Kvien, 2006) and good thermal stability (Li, Sirviö, Haapala, & Liimatainen, 2017). These favorable properties make nanocelluloses a promising resource in advanced applications such as UV-absorbing fillers for nanocomposites, (Sirviö, Visanko, Liimatainen et al., 2016) substrates for organic solar cells, (Zhou et al., 2014) agents for mineral flotation (Laitinen et al., 2014, 2016) and stabilizers of oil-water emulsions (Ojala, Sirviö, & Liimatainen, 2016).

Typically, CNFs are produced through a mechanical nanofibrillation procedure (e.g., refining, grinding, and homogenization), which requires a significant amount of energy due to the highly ordered hydrogen bond network of cellulose (Baati, Magnin, & Boufi, 2017; Sirviö, Hasa et al., 2015). Nevertheless, the high energy consumption can be reduced with the use of chemically modified (Liimatainen, Visanko, Sirviö, Hormi, & Niinimäki, 2012; Liimatainen et al., 2014; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006; Selkälä, Sirviö, Lorite, & Liimatainen, 2016), enzyme-assisted (Henriksson, Henriksson, Berglund, & Lindström, 2007; Shahid, Mohammad, Chen, Tang, & Xing, 2016), or solvent-disintegrated (Li et al., 2017; Sirviö, Visanko et al., 2015) pretreatment approaches (Siró & Plackett, 2010a). Unlike CNFs, CNCs can be conventionally fabricated by simple acidic (e.g., sulfuric (Bondeson, Mathew, & Oksman, 2006), hydrochloric (Yu et al., 2013), or phosphoric acid (Camarero Espinosa, Kuhnt, Foster, & Weder, 2013)) hydrolysis of the amorphous regions of cellulose, which releases the hard crystalline parts of cellulose. However, there are noticeable limitations to acidic hydrolysis methods, such as material corrosion, sensitive reaction conditions, low production yield (Corrêa, de Moraes Teixeira, Pessan, & Mattoso, 2010; Lu et al., 2016), and fiber aggregation (Araki, Wada, Kuga, & Okano, 1998). Therefore, oxidation-based methods such as TEMPO- (Qin, Tong, Chin, & Zhou, 2011), persulfate (Leung et al., 2011; Zhang et al., 2016) and periodate oxidation (Visanko et al., 2014) have been developed not only to compensate for the shortcomings of acidic hydrolysis methods, but also to expand functionalized CNC production (Montanari, Roumani, Heux, & Vignon, 2005; Sirviö, Visanko, Heiskanen, & Liimatainen, 2016; Visanko et al., 2014).

The introduction of cationic groups on cellulose fibers can enhance nanocellulose production and prevent the aggregation of nanocelluloses due to electrostatic repulsion (Visanko et al., 2014). In addition, introduction of cationically charged groups combined with alkyl chains, such as aminated structures, to the hydrophilic backbone of cellulose can result in the formation of amphiphilic nanocelluloses, which have potential for use as a stabilizer in oil-water emulsions (Visanko et al., 2014), flocculation agent in dewatering (Suopajarvi, Sirviö, & Liimatainen, 2017), or a colloid aggregation agent (Liimatainen et al., 2014). Previously, cationized nanocelluloses have been synthesized in epoxypropyltrimethylammonium chloride (Hasani, Cranston, Westman, & Gray, 2008) imidazolium, (Eyley & Thielemans, 2011) pyridinium (Jasmani, Eyley, Wallbridge, & Thielemans, 2013) and water (Hua et al., 2014; Sirviö et al., 2014b; Sirviö, Honka, Liimatainen, Niinimäki, & Hormi, 2011; Yang & van de Ven, 2016).

DESs have been used as alternative green routes to produce both non-derivatized (Laitinen, Suopajarvi, Österberg, & Liimatainen, 2017; Li et al., 2017; Sirviö, Visanko et al., 2015; Suopajarvi, Sirviö, & Liimatainen, 2017) and anionic (Laitinen, Ojala, Sirviö, & Liimatainen, 2017; Selkälä et al., 2016; Sirviö, Visanko, Liimatainen et al., 2016; Sirviö & Visanko, 2017) nanocelluloses, but there was very few reports about its use for the fabrication of cationized nanocelluloses (Sirviö, 2018). Thus, to the best of our knowledge, this is the first time that a recyclable and effective DES was developed to produce cationic nanocelluloses. In this work, a DES produced using aminoguanidine hydrochloride and glycerol (AhG) was used as a reaction medium and reagent (aminoguanidine hydrochloride) for cationization of dialdehyde cellulose (DAC). Birch cellulose was first oxidized to DAC using recyclable sodium periodate (Jin, Li, Xu, & Sun, 2015; Liimatainen et al., 2013; Zhang, Jiang, Dang, Elder, & Ragauskas, 2008) and then cationized by the AhG DES to produce cationic dialdehyde celluloses (CDACs) under different temperatures and reaction times. The CDACs that were synthesized at 70 °C for 10 min were selected and further mechanically nanofibrillated to obtain cationized nanocelluloses. The recyclability and yield of the DES were analyzed. The charge densities of CDACs were investigated by polyelectrolytic titration, and attenuated total reflection infrared (ATR-IR) spectroscopy was used for the chemical characterization of celluloses. Cationized nanocelluloses were characterized by transmission electron microscopy (TEM).

## 2. Materials and methods

### 2.1. Materials

Bleached kraft birch (*Betula pendula*) pulp sheets were used as cellulose raw material after they were disintegrated in deionized water. The properties of the pulp have been determined in a previous study (Sirviö et al., 2011). Lithium chloride (99%) and sodium periodate (> 99%) were obtained from Sigma Aldrich (Germany) to produce dialdehyde cellulose. Ethanol (96%) and glycerol (97%) (VWR, France) and aminoguanidine hydrochloride (> 98%) (Tokyo Chemicals Industry, Japan) were used for the cationization of dialdehyde cellulose. Sodium polyethylene sulfonate (PES-Na) from BTG (UK) was used as a polyelectrolyte to determine the cationic charge. Uranyl acetate dihydrate (98%) was from Polysciences (Germany). Polylysine solution (0.01%) was from Sigma Aldrich (Germany). Deionized water was also used throughout the study.

### 2.2. Synthesis of CDACs in the AhG DES

DAC was obtained from birch pulp by a slightly modified version of the sodium periodate oxidation method reported previously (Dash, Elder, & Ragauskas, 2012; Sirvio, Hyvakko, Liimatainen, Niinimäki, & Hormi, 2011). Briefly, 10 g (abs.) of birch pulp was diluted with 1000 g of deionized water, and the suspension was heated to a final temperature of 55 °C or 75 °C in an oil-bath system. Following this, 18 g of lithium chloride (LiCl) and 8.2 g of sodium periodate (NaIO<sub>4</sub>) were added and left to react with cellulose for 3 h at their respective temperatures. The mixed reaction suspensions were fully covered with an aluminum foil to avoid light-induced decomposition of periodate. The products were filtered, washed with 1000 ml of a 50:50 ethanol:water solution, mixed in 500 ml ethanol twice for 15 min, and filtrated. According to the reaction temperature (55 °C or 75 °C), the DAC products were labeled as DAC55 or DAC75.

The AhG DES was prepared by mixing 75 g aminoguanidine hydrochloride and 125 g glycerol in a molar ratio of 1:2 in a Scott bottle. The mixture was preheated at 90 °C in an oil bath to obtain a clear liquid, and then adjusted to the desired reaction temperatures (70, 80, 90, and 100 °C). Following this, 10 g (abs.) DAC55 or DAC75 was added into the DES, which was stirred continuously with a magnetic bar for a set of reaction times (5, 10, 15, 30 and 60 min) at the desired

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