



# Room-temperature dissolution and chemical modification of cellulose in aqueous tetraethylammonium hydroxide–carbamide solutions

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Received: 7 October 2019 / Accepted: 1 December 2019 / Published online: 7 December 2019  
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**Abstract** The room-temperature dissolution of cellulose in aqueous tetraethylammonium hydroxide (TEAOH) in the presence of carbamides (ureas) was investigated. Without carbamide, 35 wt% TEAOH was able to dissolve cellulose (microcrystalline cellulose) up to 3 wt%, whereas carbamides—such as urea, *N*-methylurea, *N*-ethylurea, 1,3-dimethylurea, and imidazolidone—were able to improve the dissolution of cellulose. At 5 wt% cellulose concentration, the highest carbamide contents in the solvent still able to dissolve cellulose within 1 h were 56 and 55 wt% of 1,3-dimethylurea and *N*-methylurea, respectively. When using urea, up to 15% of cellulose could be dissolved in a solution containing 22 wt% of urea. To demonstrate the possibility of the use of a carbamide-based solvent in cellulose modification, cationic cellulose was produced using glycidyltrimethylammonium chloride (GTAC). At a molar ratio of 1:3 of cellulose and GTAC, all the studied TEAOH–

carbamide solvents produce cationic cellulose with higher charge density compared to the reference NaOH–urea solvent.

**Keywords** Cellulose · Dissolution · Carbamate · Tetraethylammonium hydroxide · Cationization

## Introduction

The replacement of oil-based materials, such as plastic, with the bioderived counterpart is highly desirable because of the disadvantageous properties of plastic (Shen et al. 2010). In particular, the biodegradability of many oil-based materials is poor, leading to a severe environmental hazard because of the accumulation of solid waste in soil and water systems (Siracusa et al. 2008). Furthermore, several starting chemicals (i.e., monomers) for oil-based plastic are toxic. The toxicity of monomers can lead to possible hazards during manufacturing, and the remaining unreacted monomers are a source of secondary pollution when in use (Lithner et al. 2012). In addition, at the current consumption rate, oil cannot be described as a renewable resource (Owen et al. 2010).

The use of biomass derived monomers for bioplastic synthesis is one part of the solution to replace oil-based materials (Raquez et al. 2010; Chen and Patel 2012). Additionally, a vast variety of polymers already

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**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10570-019-02907-x>) contains supplementary material, which is available to authorized users.

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occurring in nature can serve as an important starting point for plastic replacement (Vieira et al. 2011). However, unlike many synthetic plastics, most natural polymers, such as carbohydrates, have poor formatibility; that is, they cannot be melted (Scandola et al. 1991) and have poor solubility in common solvents (Guo et al. 2017). Poor formatibility is particularly severe with cellulose, which as such could be an ideal plastic replacement because of its wide availability; that is, cellulose is the most abundant natural polymer on Earth (Wang et al. 2012). Generally, it is described that cellulose has a melting point higher than its degradation temperature (Krumm et al. 2016). Therefore, conventional melting cannot be used for cellulose processing.

Despite the poor dissolution of cellulose in common solvents (Olsson and Westm 2013), several types of solvents have been investigated in shaping (e.g., forming of yarns and films) or chemical modifications of cellulose. *N*-methylmorpholine-*N*-oxide is among the most well-known cellulose solvents, which is used on an industrial scale to produce regenerated cellulose fibers (Lyocell fibers) (Perpelkin 2007). Cellulose can be dissolved in organic solvents, such as *N,N*-dimethylacetamide (DMAc) in the presence of lithium chloride (Dawsey and McCormick 1990). In addition, tetrabutylammonium fluoride (Östlund et al. 2009) and acetate (Idström et al. 2017) have been used to dissolve cellulose in dimethyl sulfoxide (DMSO). Even acetone can be used to dissolve cellulose in the presence of triethyloctylammonium chloride (Kostag et al. 2014). However, these systems have some disadvantages, such as instability, volatility, and toxicity.

Ionic liquids are a novel class of solvents capable of dissolving various materials and chemicals, including cellulose (Isik et al. 2014). One drawback of using ionic liquids is their sensitivity to moisture; that is, the presence of water can decrease cellulose solubility (Mazza et al. 2009), although it should be noted that in some cases water can even act as a cosolvent (Parthasarathi et al. 2015). Sensitivity to moisture can be problematic with cellulose because of its high hygroscopicity, and completely dry conditions are hard to accomplish. In addition, some ionic liquids exhibit a certain level of toxicity (Thuy Pham et al. 2010), are poorly biodegradable (Jordan and Gathergood 2015), and are not completely innocent solvents; that is, they cause the degradation (Yang et al. 2019)

and chemical modification (Clough et al. 2014) of cellulose.

One way to circumvent the moisture-related problem in the dissolution of cellulose is the use of aqueous solvents, as they can tolerate higher moisture fluctuations. Aqueous NaOH and LiOH solutions in the presence of urea are especially interesting solvents, as they consist mainly of water, are cheap, and have low toxicity. (The main hazards are due to the alkalinity of the solvents) (Cai and Zhang 2005.) However, even in the presence of urea, both NaOH and LiOH exhibit relatively poor solvent capacity; that is, a small amount of cellulose can be dissolved and high-molecular-weight cellulose is poorly soluble (Le Moigne and Navard 2009). In addition, low temperature (around  $-12\text{ }^{\circ}\text{C}$ ) is requested for dissolution, somewhat restricting the use of aqueous NaOH and LiOH solutions in the dissolution of cellulose on an industrial scale.

Hydrated ionic liquids, such as aqueous alkylammonium (Ema et al. 2014; Zhong et al. 2017) and alkylphosphonium hydroxides (Hyväkkö et al. 2014), are another class of solvents studied in the case of cellulose processing. Due to their amphiphilic properties of cellulose (Lindman et al. 2010), amphiphilic alkylammonium and alkylphosphonium hydroxides are shown to be efficient solvent for cellulose (Wei et al. 2017). Compared to alkaline metal hydroxides, ammonium and phosphonium hydroxides can be used at room temperature. For example, tetrabutylphosphonium hydroxide (TBPOH) can dissolve up to 20% cellulose (microcrystalline cellulose, MCC) at room temperature (Abe et al. 2012). Similar to NaOH and LiOH, the presence of urea can improve the dissolution of cellulose (Wei et al. 2017; Zhang et al. 2019). However, there is still lack of comprehensive studies related to urea and other carbamides in the dissolution of cellulose, especially when high concentrations of carbamides are used. Although tetraalkylammonium hydroxides can biodegrade (Singh and Prasad 2019), they are still relatively toxic and their partial replacement with less harmful chemicals (e.g., carbamides, such as urea) is desirable. In addition, many carbamides are cheaper compared to ammonium and phosphonium hydroxides, and in some cases, they can be produced directly from carbon dioxide (Chaudhari et al. 1991; Xiang et al. 2012).

Tetraethylammonium hydroxide (TEAOH) has been previously used for cellulose dissolution (Powers

and Bock 1935; Abe et al. 2015), however, maximum of 3 wt% cellulose solution was obtained at room temperature (Sirviö et al. 2017). In this study, MCC solubility in TEAOH in the presence of various carbamides was investigated. In addition, thiocarbamide (thiourea) and DMSO were studied as a reference. Nuclear magnetic resonance (NMR) spectroscopy was used to study the possible mechanism for the dissolution of cellulose. Furthermore, the homogeneous chemical modification of cellulose in TEAOH–carbamide solvent was studied to produce cationic cellulose.

## Materials and methods

### Materials

Avicel PH-101 MCC (particle size  $\sim 50 \mu\text{m}$ ), TEAOH (35 wt% in water), *N*-methylurea (MU, 97%), *N*-ethylurea (EU, 97%), 1,3-dimethylurea (1,3-DMU,  $\geq 95.0\%$ ), 1,1-dimethylurea (1,1-DMU, 99%), *N*-phenylurea (97%), and thiourea ( $\geq 99.0\%$ ) were obtained from Sigma Aldrich (Germany); imidazolidine (IMIDO,  $> 97.0\%$ ), tetramethylurea ( $> 98.0\%$ ), glycidyltrimethylammonium chloride (GTAC, 80 wt% in water), and tetraethylammonium chloride (TEACl,  $> 98.0\%$ ) from TCI (Belgium); urea ( $\geq 97\%$ ) from Borealis Biuron (Austria); and DMSO ( $\geq 99.5\%$ ), NaOH, and ethanol (96%) from VWR (Finland). The bleached birch (*Betula verrucosa*) chemical pulp and the dissolving pulp (softwood) were obtained as dry sheets and their chemical compositions are presented in the previous study (Sirvio et al. 2011).

### Dissolution of cellulose

TEAOH-based solvent was prepared by stirring a desired amount of components in a glass bottle, followed by mixing at room temperature (23 °C). If a clear liquid was not observed after 1 h of mixing, the sample was heated at 60 °C for a maximum of 1 h, followed by cooling to room temperature.

The initial study was conducted by mixing MCC with TEAOH-based solvents to produce 5 wt% cellulose solution. Dissolution was confirmed by optical microscope. If a clear liquid was obtained, further studies were conducted to produce 7.5, 10.0, 12.5, and

15 wt% solutions. Apart from the 15 wt% cellulose concentration, all the mixing was done using a magnetic stirrer and 15 wt% solutions using an overhead stirrer. Cellulose was regenerated and washed using ethanol until suspension became neutral. Sample was dried in an oven at 60 °C for further characterization.

### Recycling of TEAOH-based solvent

Cellulose was dissolved in TEAOH–urea at a molar ratio of 1:2, as described above, to produce 10 g of 5 wt% cellulose solution. Cellulose was regenerated with 10 mL of ethanol, filtrated, and washed with another 10 mL of ethanol. The regenerated cellulose was collected and dispersed in 10 mL of ethanol for 15 min, followed by filtration and final washing with 10 mL of ethanol. The filtrate was collected and ethanol was removed by a rotary evaporator at 60 °C under vacuum. The regenerated TEAOH–urea was directly used for the dissolution of cellulose.

### Degree of polymerization

The average degree of polymerization (DP) was determined by limiting viscosity, as measured in copper ethylenediamine (CED) solution according to the ISO 5351 standard (Liimatainen et al. 2011; Sirviö and Heiskanen 2017).

### NMR measurements

For NMR measurements, 1 mL of TEAOH–urea solution at a molar ratio of 1:2 was prepared, followed by the addition of 0.1 mL of D<sub>2</sub>O. Pure TEAOH and urea solutions were prepared in a similar way, but the missing component was replaced with deionized water. Cellulose solutions at 5.0 and 7.5 wt% MCC concentrations were produced in a similar way. The sample was placed in a 5 mm NMR tube and the <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Ascend 400 MHz spectrometer at ambient temperature (23 °C).

### Elemental analysis of regenerated cellulose

The nitrogen content of the regenerated cellulose was measured using the PerkinElmer CHNS/O 2400 Series

II elemental analyzer to confirm the purity of regenerated cellulose.

#### Chemical characterization of regenerated cellulose

Chemical characterization of the original MCC and regenerated cellulose was performed using diffusion reflectance Fourier transform (DRIFT) infrared spectroscopy. DRIFT spectra were collected from the dried samples with a Bruker Vertex 80v spectrometer (USA). The spectra were obtained in the 600–4000  $\text{cm}^{-1}$  range and 40 scans were taken from each sample at a resolution of 2  $\text{cm}^{-1}$ .

#### Viscosity of cellulose solutions

For viscosity measurements, 5 wt% MCC solutions were produced and viscosities were determined by the TA Instruments Discovery HR-1 hybrid rheometer, using cone–plate geometry (cone diameter of 40 mm and cone–plate angle of 1.999°). All measurements were conducted at 25 °C at a shear rate of 20–900  $\text{s}^{-1}$ .

#### Homogenous cationization of cellulose

At first, 5 wt% cellulose solutions were produced by dissolving 0.2 g of MCC in TEAOH–carbamide solutions (Table 2). GTAC was added dropwise into cellulose solutions at a molar ratio of 1:3 of cellulose and GTAC, and the reaction was allowed to proceed for 24 h at room temperature (23 °C). The products were precipitated with ethanol, followed by centrifugation (Avanti J-26 XPI, Beckman Coulter, USA) at 8000 rpm for 10 min at 5 °C. The supernatant was discarded, and the solid was mixed with ethanol and centrifuged again. Washing and centrifugation was repeated until the supernatant remained neutral after two sequential washing steps. The products were collected and dried in an oven at 60 °C.

Aqueous NaOH (7 wt%) and urea (12 wt%) were used as the reference solution. MCC was dissolved in NaOH–urea solution, using the freeze–thaw method described in literature (Schmidt et al. 2014). Cationization was done in a similar manner as described above for TEAOH–carbamide solutions.

#### Charge density of cationic cellulose

The charge density of cationic cellulose was determined using polyelectrolyte titration (Li et al. 2018). During titration, the sample was dissolved in water to produce 0.01 wt% solution and the consumption of the titrant (sodium polyethene sulfonate [PES-Na; BTG Müttek GmbH, Germany]) was monitored using the MüttekPCD 03 particle charge detector (USA).

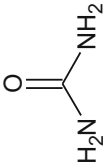
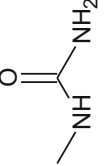
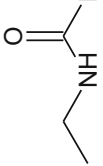
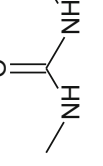
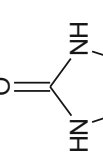
## Results and discussion

#### TEAOH and carbamide-based solvents

The previous studies have shown that aqueous 35 wt% TEAOH can dissolve up to 3% of the dissolving pulp (Sirviö et al. 2017). Although low-molecular-weight MCC can have higher dissolution in various solvents compared to high-molecular-weight wood pulp (Qi et al. 2008), the maximum dissolution of MCC in TEAOH was found to be the same as that with the dissolving pulp, 3%. Therefore, to improve the relatively poor dissolution ability, TEAOH was mixed with various carbamides and the dissolution ability of these mixtures was investigated. The molar ratio of TEAOH and carbamides varied from 1:2 to 1:7. In addition to carbamides, thiourea was investigated as thiocarbamide has been previously shown to improve the dissolution of cellulose (and other polysaccharides) in various solvents (Zhang et al. 2002; Sharma et al. 2013). Moreover, DMSO was studied as a reference as it has been widely used as a solvent to dissolve cellulose together with various salts (Östlund et al. 2009; Chen et al. 2018; Kostag and El Seoud 2019) and as a cosolvent to decrease the viscosity of cellulose solutions in ionic liquids (Rinaldi 2010; Ferreira et al. 2019). The chemical formulas of all the studied chemicals are presented in Fig. S1 in the ESI†.

Of the studied carbamides, urea, MU, EU, 1,3-DMU, and IMIDO were able to produce a clear liquid with TEAOH at least at one studied molar ratio (Table 1). On the contrary, phenylurea did not form a clear liquid with TEAOH, possibly because of the presence of a bulky hydrophobic phenyl group. Surprisingly, 1,1-DMU (the isomer of 1,3-DMU) was not able to form a clear liquid with TEAOH at any molar ratio, whereas clear liquids were obtained with 1,3-DMU at all studied molar ratios. A possible

**Table 1** Carbamides capable of improving the dissolution of cellulose at least at one concentration (+ = dissolution, – = no dissolution), molar ratio of carbamide and TEAOH, mass percentage of carbamide and water, and DP of the regenerated cellulose

Carbamide	Constitution of solvents		Cellulose concentration during dissolution					DP of regenerated cellulose <sup>d</sup>			
	Moles of carbamide per mol of TEAOH	Carbamide (wt%)	TEAOH (wt%)	H <sub>2</sub> O (wt%)	Cellulose concentration during dissolution						
					5.0 wt%	7.5 wt%	10.0 wt%		12.5 wt%	15.0 wt%	
 Urea	2	22	27	51	+	+	+	+	+	+	378
	3	30	24	46	+	+	+	–	–	–	– <sup>c</sup>
	4	36	23	41	+	+	+	–	–	–	– <sup>c</sup>
	5	42	20	38	+	+	–	–	–	–	– <sup>c</sup>
	6	46	19	35	+	+	–	–	–	–	– <sup>c</sup>
	2	26	26	48	+	+	+	+	–	–	383
 Methylurea	3	35	22	43	+	–	–	–	–	– <sup>c</sup>	
	4	41	21	38	+	–	–	–	–	–	– <sup>c</sup>
	5	47	18	35	+	–	–	–	–	–	– <sup>c</sup>
	6	51	17	32	+	–	–	–	–	–	– <sup>c</sup>
	7	55	16	29	+	–	–	–	–	–	– <sup>c</sup>
	2	30	24	46	+	+	+	+	–	–	390
 Ethylurea	3	39	21	40	–	–	–	–	–	– <sup>c</sup>	
	4	46	19	35	–	–	–	–	–	–	– <sup>c</sup>
	5	51	17	32	–	–	–	–	–	–	– <sup>c</sup>
	6	56	15	29	–	–	–	–	–	–	– <sup>c</sup>
	7	59	15	26	–	–	–	–	–	–	– <sup>c</sup>
	2	29	25	46	+	+	+	+	–	–	383
 1,3-Dimethylurea	3 <sup>a</sup>	38	22	40	–	–	–	–	–	– <sup>c</sup>	
	2	30	24	46	+	+	+	–	–	–	384
	3	39	21	40	+	–	–	–	–	–	– <sup>c</sup>
	4	46	19	35	+	–	–	–	–	–	– <sup>c</sup>
	5	51	17	32	+	–	–	–	–	–	– <sup>c</sup>
	6	56	15	29	+	–	–	–	–	–	– <sup>c</sup>
 Imidazolidone	7	59	15	26	–	–	–	–	–	– <sup>c</sup>	
	2	29	25	46	+	+	+	+	–	–	383
	3 <sup>a</sup>	38	22	40	–	–	–	–	–	– <sup>c</sup>	

<sup>a</sup>Formed after heating at 60 °C<sup>b</sup>Mixed using an overhead stirrer<sup>c</sup>Not determined<sup>d</sup>DP of MCC = 373

reason for different behaviors of two dimethylurea isomers is discussed later. The systems that were not able to produce a clear liquid were heated for 1 h at 60 °C. However, only IMIDO with a molar ratio of 1:3 formed a liquid that remained clear when cooled to room temperature. Others either remained turbid suspensions at higher temperatures or precipitated after cooling.

MU and 1,3-DMU were only carbamides able to produce a clear liquid with TEAOH at the whole investigated molar range, whereas no clear liquid was observed with urea at a molar ratio of 1:7 of TEAOH and urea. This might be due to the higher hydrophobicity of MU and 1,3-DMU compared to urea, which helped them to interact with TEA cation. On the contrary, EU with a longer alkyl chain and IMIDO with a cyclic structure produced a clear liquid only at a molar ratio of 1:2 at room temperature.

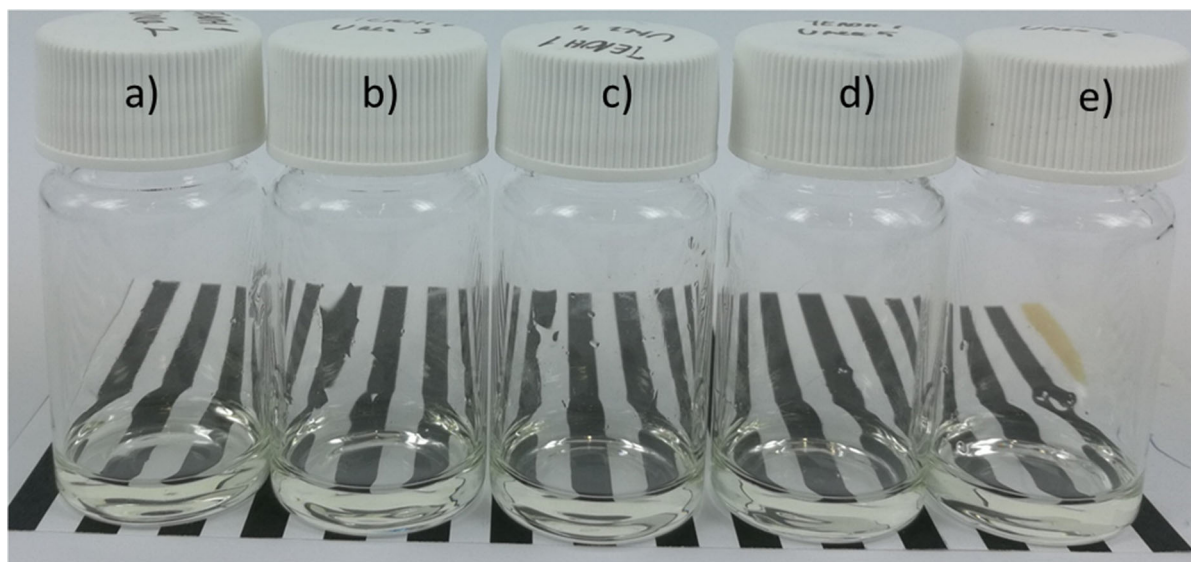
#### Dissolution of cellulose

The systems that produced a clear liquid were then mixed with MCC to produce 5 wt% cellulose solution (Table 1). All of the dissolution experiments were conducted at room temperature, and the maximum dissolution time was set to 1 h. The examples of 5% cellulose solutions in urea-containing solvents are presented in Fig. 1, whereas other solutions are presented in Fig. S2 in the ESI†. From Table 1, it

can be seen that of the studied solvents, the highest carbamide contents in solvent mixture still able to dissolve 5 wt% cellulose were 55 and 56 wt% of MU and 1,3-DMU (corresponding to a molar ratio of 1:7 and 1:6, respectively, of TEAOH and carbamide). Surprisingly, TEAOH with either thiourea or DMSO failed to provide a clear liquid with cellulose (Fig. S2e and f). In addition, cellulose could not be dissolved in TEAOH together with tetramethylurea (Fig. S2d).

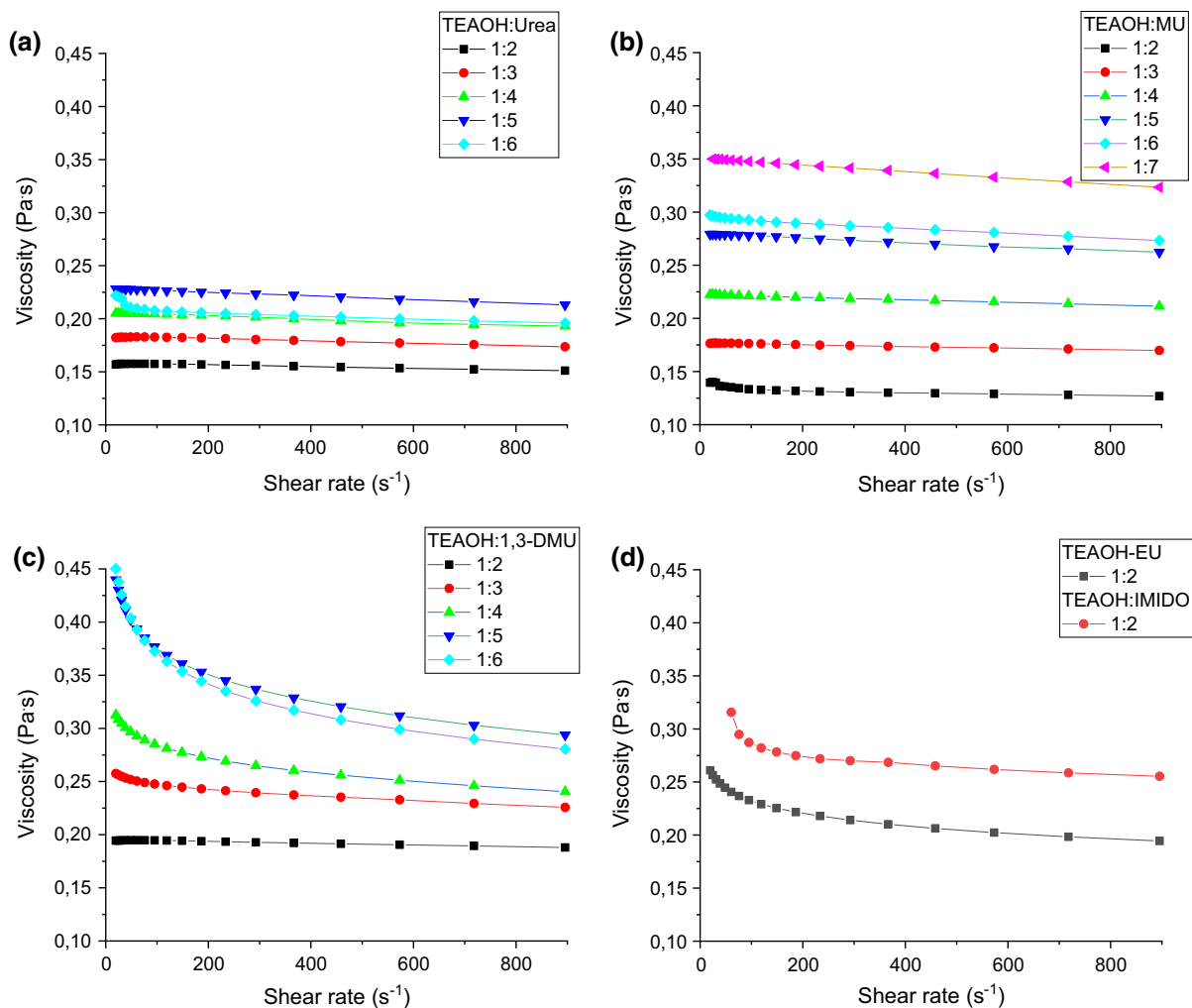
#### Viscosity of 5 wt% cellulose solutions

The viscosities of 5 wt% cellulose solutions in different solvents are presented in Fig. 2a–d. The lowest viscosity of TEAOH–carbamate solutions at 5 wt% cellulose concentration was observed with MU at a molar ratio of 1:2 (Fig. 2b). However, the viscosity of MU-containing solutions notably increased when the amount of MU was increased. On the contrary, only a minor increase in the viscosity of cellulose solution could be seen in urea-containing solutions when the amount of urea was increased (Fig. 2a). For example, at a shear rate of  $20 \text{ s}^{-1}$ , the viscosity of 5 wt% cellulose solution increased from 0.16 to 0.22 Pa s when the molar amount of urea was increased from 2 to 6, whereas at the same shear rates and molar concentrations, the viscosities of MU-containing solvents were 0.14 and 0.29 Pa s.



**Fig. 1** Cellulose solutions (5 wt%) in TEAOH–urea at molar ratios of 1:2 (a), 1:3 (b), 1:4 (c), 1:5 (d), and 1:6 (e)





**Fig. 2** The viscosities of 5 wt% MCC solutions in **a** urea-, **b** MU-, **c** 1,3-DMU-, and **d** EU- and IMIDO-containing solvents at different carbamide concentrations

Most of the 5 wt% cellulose solutions with urea or MU exhibited Newtonian or only minor shear-thinning properties, which have been observed, for example, in cellulose solution in imidazolium-based ionic liquids (Sescousse et al. 2010). In contrast, a notable shear-thinning behavior was observed with 1,3-DMU, especially at the carbamide concentrations higher than 3 relative to TEAOH in mol ratio (Fig. 2c). In addition, minor shear thinning was also observed in both EU- and IMIDO-containing solvents (Fig. 2d). The shear thinning is typical behavior of many polymeric solutions (Bird and Hassager 1987), as in state the interaction between polymer chains causes the increase in viscosity, whereas increase in shear force decreases viscosity (Ryder and Yeomans 2006).

Therefore, due to the different interaction of polymers at steady state compared to the situation when shear force is applied, many polymer solutions are non-Newtonian fluids.

The different viscosity behaviors of cellulose solution indicate the altered orientations of cellulose chains in carbamide-containing solutions. Although both 1,3-DMU and EU are able to help with the dissolution of cellulose, a steady-state hydrophobic characteristic of these chemicals might lower their interaction with cellulose, causing cellulose chains to have a better interaction with each other. The interaction between cellulose chains causes entanglement, that is, the formation of cellulose aggregates. These aggregates are opened and elongated when exposed to

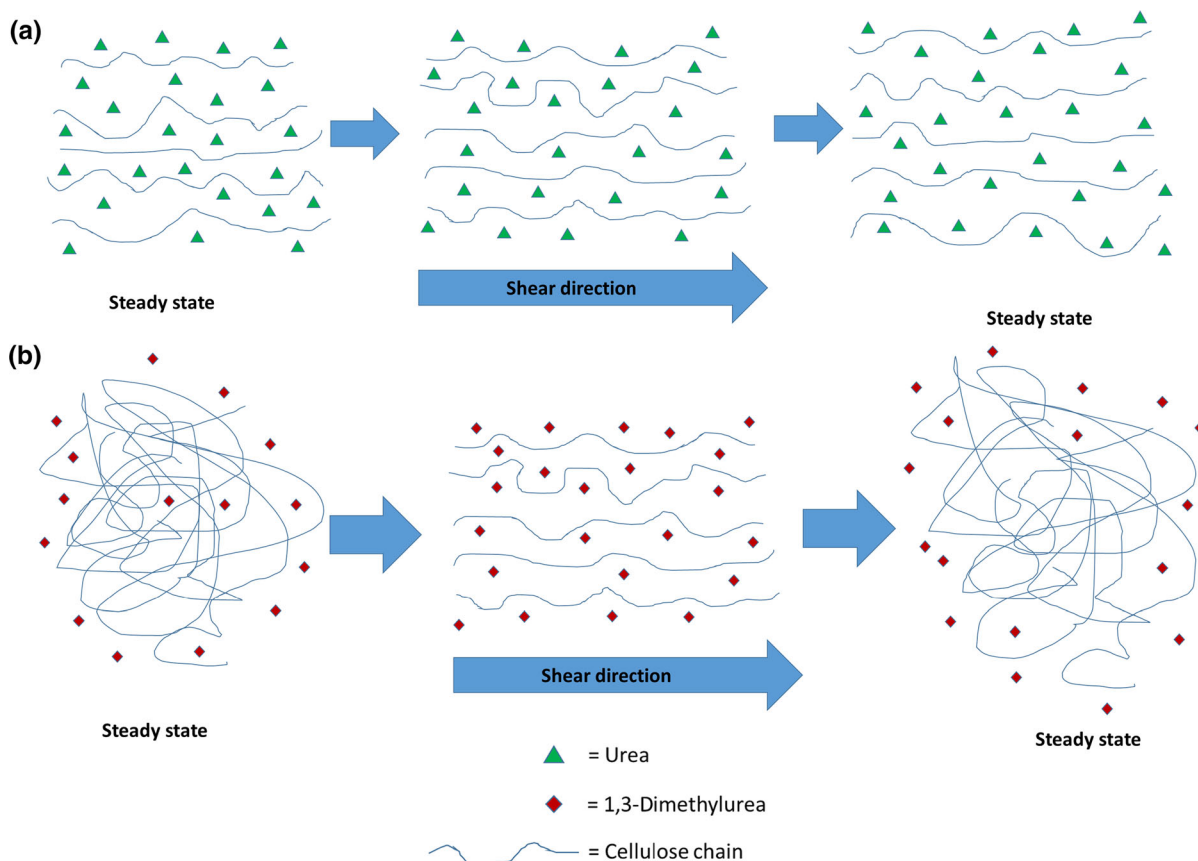
shear force because of the mechanical force. On the contrary, less hydrophobic urea and MU are able to stabilize cellulose chains more efficiently, thus preventing aggregation. A schematic illustration of the cellulose chain behavior in urea- and 1,3-DMU-containing solutions is presented in Fig. 3.

#### Dissolution of higher MCC concentrations and high-molecular-weight cellulose

Although 5 wt% cellulose solution has been efficiently used, for example, to produce cellulose filaments, which were further used to produce carbon fibers by carbonization (Kuzmina et al. 2017), higher cellulose concentrations are desirable to fabricate strong regenerated cellulose fibers and films. Therefore, the production of solutions with higher cellulose concentrations was studied. It can be seen from

Table 1 that although 1,3-DMU has the widest molar ratio range for the dissolution of 5 wt% cellulose, a maximum of 7.5 wt% cellulose solution could be obtained using a molar ratio of 1:2 of TEAOH and 1,3-DMU. On the contrary, at a molar ratio of 1:2, IMIDO-containing solvent systems could dissolve up to 10 wt% cellulose, whereas both EU and MU could be used to obtain 12.5 wt% cellulose solution. The maximum dissolution capacity was observed when using TEAOH–urea with a molar ratio of 1:2. This solvent could dissolve 15 wt% of MCC at room temperature within 1 h. It should be noted that although all of the other dissolution experiments were conducted using a magnetic stirrer, an overhead mechanical stirrer was used to produce 15 wt% cellulose solution because of the increased viscosity.

While solvents such as ionic liquids can dissolve significantly higher amounts of cellulose (1-ethyl-3-



**Fig. 3** Schematic illustration of the cellulose chain behavior in **a** urea- and **b** 1,3-DMU-containing solvents at steady states and when shear force is applied, explaining the different viscosity

behaviors of urea and 1,3-DMU, depending on **a** elongated or **b** aggregated structure at a steady state



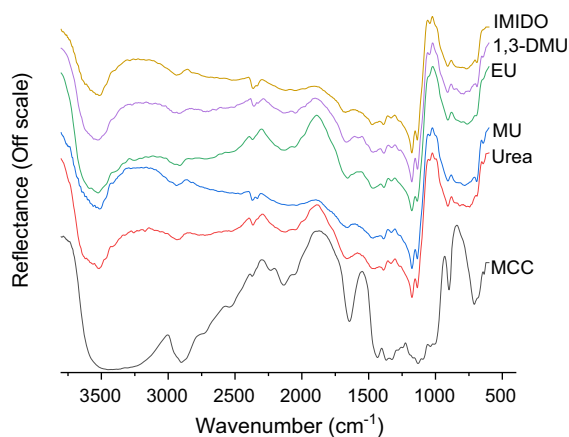
methylimidazolium acetate can dissolve up to 35.2%), they usually require an elevated temperature. DMAC/LiCl can dissolve cellulose at room temperature; however, a solvent exchange-based pretreatment is required. Many aqueous ammonium and phosphonium hydroxides are able to dissolve cellulose at room temperature. The highest room temperature dissolution capacity has been observed with TBPOH, which is able to dissolve 20 wt% cellulose within 5 min at room temperature (Abe et al. 2012). Cellulose solution up to 15.7 wt% has been obtained using *N*-methylimidazole with tetrabutylammonium propionate at 25 °C, whereas 7 wt% cellulose solution has been investigated previously with tetrabutylammonium hydroxide–urea solution, with a final urea concentration of 29 wt% (Wei et al. 2017). (For a comprehensive discussion on the dissolution of cellulose in tetraalkylammonium and phosphonium salt, please see the previous review article (Kostag et al. 2018).) Therefore, in light of the previous publication, it can be concluded that TEAOH with carbamides is a potential green solvent for cellulose because of the comparable dissolution capacity with other known cellulose solvents.

In addition to the low-molecular-weight MCC, 5 wt% could be obtained using the dissolving pulp with a DP of 1800 with TEAOH and urea at a molar ratio of 1:2. However, some fibers were still visible at higher concentrations. In addition, no complete dissolution at 5% cellulose concentration was observed with the birch pulp having a DP of 3600. Lower dissolution of the wood pulp indicates that the dissolution of cellulose depends on the DP of the starting material. It was observed that the viscosity of the solution produced with wood pulps was significantly higher compared to solutions containing MCC; thus, it can be assumed that the mass transfer between cellulose and solvent was restricted, resulting in poor solubility. It should be noted that maximum mixing time for high DP cellulose was set to one hour and the longer and more intensively mixing might be used to improve the solubility.

#### Analysis of regenerated cellulose

The dissolution and regeneration of cellulose can decrease the DP of cellulose depending on the utilized solvent and dissolution conditions (e.g., temperature and time). For example, a slight decrease in the DP of

MCC has been observed with various ionic liquids (Kuzmina et al. 2017). Here, the DP of the cellulose regenerated from carbamide-based solvents was observed to be similar to that of the original MCC (Table 1). Therefore, it can be assumed that despite the high alkalinity of TEAOH, dissolution at mild conditions (1 h at room temperature) does not lead to the degradation of cellulose. In addition, the elemental analysis of the regenerated cellulose showed the absence of nitrogen, indicating that the solvents were efficiently removed during washing and no chemical modification, such as carbamation, occurred during dissolution. The regeneration of cellulose without derivatization was further confirmed by DRIFT analysis, as no carbonyl peak could be observed around 1720–1700  $\text{cm}^{-1}$  (Fig. 4) (Yin and Shen 2007; Sirviö and Heiskanen 2017). The spectra of MCC and regenerated cellulose mostly contained typical cellulose peaks; however, some shift of the peak position could be observed after regeneration typically from the transformation of cellulose I crystalline structure to cellulose II and poorly crystalline cellulose (Duchemin et al. 2015). For example, the maximum of OH region was shifted from around 3450  $\text{cm}^{-1}$  to a higher wave number (3520  $\text{cm}^{-1}$ ). (Lan et al. 2013) In addition, the peak associated to the cellulose I (the peaks at 1107, 1161 and 1430  $\text{cm}^{-1}$  related to ring asymmetric stretching, C–O–C asymmetric stretching, and CH<sub>2</sub> symmetric bending vibration) (Yang et al. 2017) disappeared after dissolution and regeneration, further indicating the no natural cellulose I allomorph

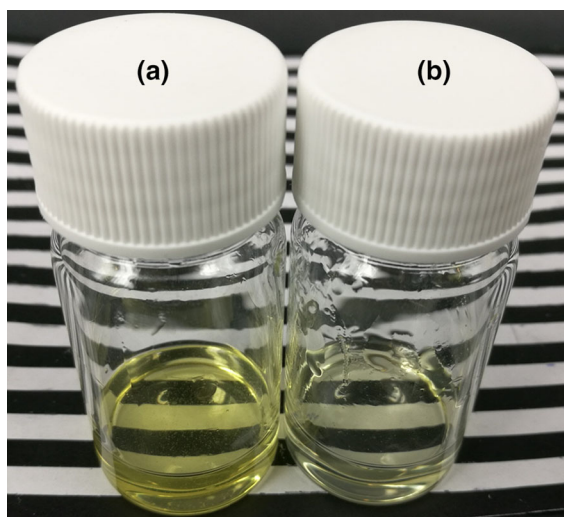


**Fig. 4** DRIFT analysis of the original cellulose (MCC) and the regenerated cellulose from TEAOH–carbamide solutions at a molar ratio of 1:2

is presented in cellulose regenerated from TEAOH-carbamate solution.

### Recycling of cellulose solvent

It has been suggested that because of the high nitrogen content, the spent tetraalkylammonium-based hydrated ionic liquids could be used as stimulants for nitrogen-deficient seaweeds (Singh and Prasad 2019). The presence of urea in these solvents could further promote feasibility of the use of the spent biomass solvent as a fertilizer. However, with respect to the ecologic and economic feasibility, recycling is the foremost way to utilize the TEAOH-carbamide solution after the dissolution and regeneration of cellulose. Previously, tetrabutylammonium (Zhong et al. 2013) and other tetraalkylammonium (Wang et al. 2018) hydroxides have been successfully recycled. Here, TEAOH-urea solution was recovered after the regeneration of cellulose with ethanol. Ethanol was removed by rotary evaporation and the obtained solution was directly used for the dissolution of cellulose. It was observed that during the removal of ethanol, slight yellowing of TEAOH-urea solution occurred (Fig. S3 in the ESI<sup>†</sup>). The yellowing indicates that some unwanted side-reactions occurred when TEAOH-urea solution was handled at an elevated temperature. Nevertheless, the recycled solution could be used for the dissolution of cellulose



**Fig. 5** Cellulose solutions (5 wt%) in the recycled (a) and fresh (b) TEAOH-urea solution (the molar ratio of TEAOH and urea was 1:2)

(Fig. 5). However, further studies should be conducted to investigate how consequent recycling affects dissolution abilities.

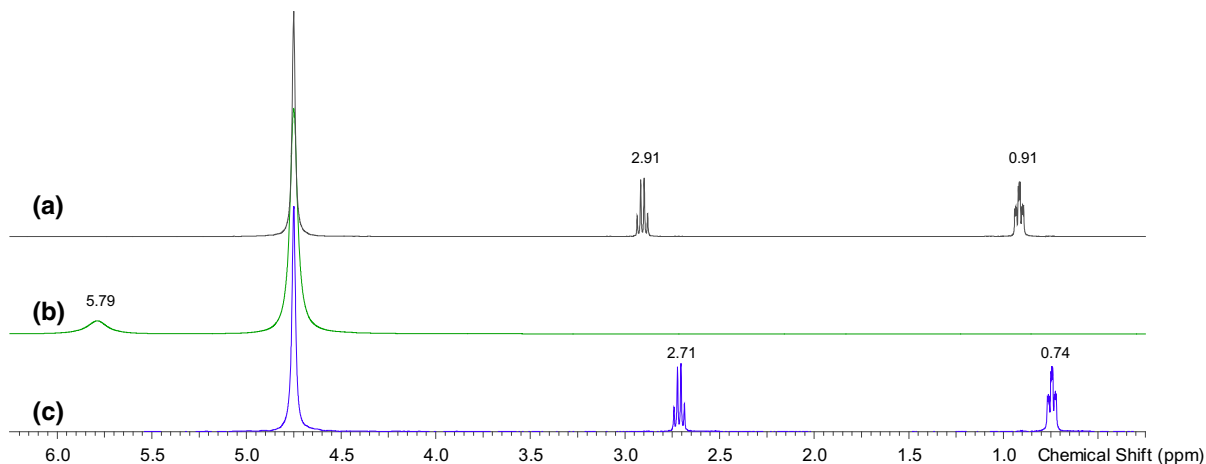
### NMR measurements

NMR measurements were performed to shed light on the formation mechanism of the solvent obtained by mixing TEAOH with carbamides and the dissolution of cellulose thereafter. From  $^1\text{H}$  NMR spectra, it can be seen that the addition of urea caused a decrease in the chemical shift of TEA cation from around 2.91 and 0.91 ppm to 2.71 and 0.74 ppm, respectively (Fig. 6). This could be due to changes in the hydration sphere (i.e., the replacement of water molecules with urea) around the cation, as proposed previously (Wei et al. 2017). In addition, the amide proton band of urea around 5.79 ppm disappeared when mixed with TEAOH. The disappearance is most likely due to the fast H-D exchange in alkaline conditions (Jiang et al. 2014). In  $^{13}\text{C}$  NMR spectra, the most notable changes when urea was mixed with TEAOH was the shift of the carbonyl band (162.8 ppm) into a slightly lower ppm value (162.0), whereas changes in the chemical shifts of carbons in TEA cation were in the range of 0.1–0.2 ppm (Fig. 7). These results indicate that there was no, or only weak, interaction between TEA cation and urea, and the small change in the carbonyl peak of urea was due to the interaction of urea with hydroxide ion.

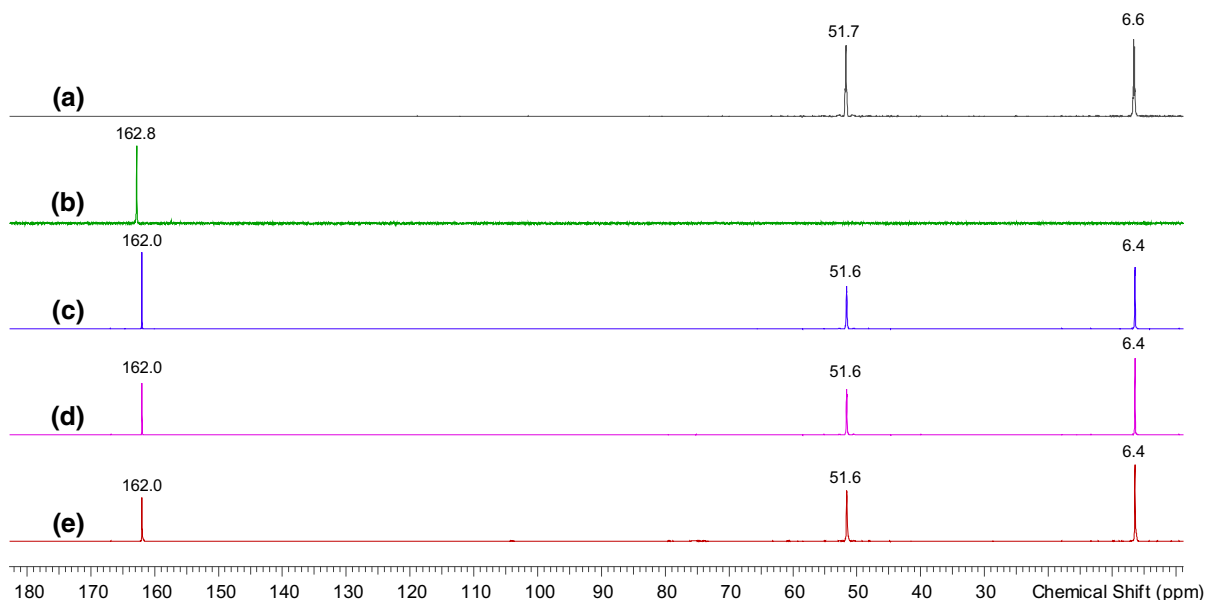
When 5% of cellulose was dissolved in TEAOH-urea at a molar ratio of 1:2, no changes in the chemical bands of urea or TEA cation could be seen in  $^{13}\text{C}$  spectra (Fig. 7d). The further increase of cellulose concentration to 7.5% showed no changes in the NMR spectra (Fig. 7e). The independence of the chemical shift of urea and TEA cation on cellulose concentration indicates that there was only a weak interaction between cellulose and either of the components in the solvent.

### Dissolution mechanism of cellulose

The effect of urea on the dissolution of cellulose has been intensively studied (Cai and Zhang 2005; Egal et al. 2008; Isobe et al. 2013; Jiang et al. 2014). The original idea of the effect of urea in the dissolution of cellulose in NaOH-urea solution was the formation of cellulose-NaOH-urea inclusion complex (Cai and



**Fig. 6**  $^1\text{H}$  NMR spectra of (a) TEAOH, (b) urea, and (c) TEAOH–urea at a molar ratio of 1:2



**Fig. 7**  $^{13}\text{C}$  NMR spectra of (a) TEAOH, (b) urea, (c) TEAOH–urea, and MCC solution in TEAOH–urea at cellulose concentrations of (d) 5 wt% and (e) 7.5 wt% (a molar ratio of 1:2 of TEAOH and urea)

Zhang 2005). Later studies have shown that, in liquid state, urea has only weak interaction (the van der Waals force) with cellulose (Xiong et al. 2014), which is also suggested by the NMR studies conducted in the current study. The weak interaction is proposed to take place with urea and the hydrophobic plane of cellulose (carbon ring), which prevents the aggregation of cellulose chains, thus stabilizing the cellulose solution (Isobe et al. 2013). Together with tetrabutylammonium hydroxide, urea is proposed to adjust the

amphiphilicity of the solvent, resulting in higher cellulose solubility (Wei et al. 2017).

There is possibility that mixing of carbamides with TEAOH would result in the formation of a deep eutectic solvent (DES) type of a solvent. Although there is only limited information on DESs that could dissolve cellulose (Kostag et al. 2018; Sirviö 2019), DESs are proposed as an alternative solvent for ionic liquids, as they both have good dissolution ability toward many chemicals. It is well known that carbamides such as urea (Abbott et al. 2003; Smith

et al. 2014; Li et al. 2017) and 1,3-DMU (Sirviö and Heiskanen 2017; Mainar et al. 2018) are able to form DESs with various components such as metal and ammonium salts. In choline chloride–urea DES, urea acts as a hydrogen bond donor and interacts with the chloride ion by the hydrogen atoms in both amide nitrogens (Ashworth et al. 2016). A similar behavior might take place when urea (or other carbamides) are mixed with TEAOH; that is, urea forms a hydrogen bond complex with the hydroxide ion. The complex is stabilized by the symmetric hydrogen bond donor ability of urea because of the presence of hydrogen in both nitrogen atoms. This assumption is reasoned by the inability of 1,1-DMU to form a clear liquid with TEAOH, as 1,1-DMU has hydrogen atoms only in second amide nitrogen. The hydrogen bond interaction between hydroxide anion and 1,1-DMU would result in asymmetric charge delocalization, which would in turn form a less stable complex. In  $^{13}\text{C}$  NMR spectra, it was observed that the carbonyl band of urea shifted to a slightly lower ppm value when mixed with TEAOH, indicating higher electron density of the carbonyl carbon. Higher electron density might originate from the interaction of urea with the high-electron-density hydroxide ion. Similarly, the poor dissolution ability of tetramethylurea containing solution towards cellulose might be explained by the inability of tetramethylurea to form hydrogen bonding with hydroxide ion. In addition, poor solubility of cellulose in thiourea (which contains two  $\text{NH}_2$  groups, similar to urea) containing solution, might be due to the thione-thiol tautomerization of thiourea (Allegretti et al. 2000), causing it to have different hydrogen bonding ability compared to carbamides.

The formation of a hydrogen bond complex with urea and hydroxide anion might also contribute to the dissolution of cellulose. It has been shown that the hydroxide ion can interact with cellulose by electrostatic force. However, this interaction is not completely stable and the cation is required to improve stability. Upon comparing sodium and lithium ions, lithium was found to be a more efficient stabilizer toward hydroxide–cellulose complex and thus cellulose has higher solubility in aqueous LiOH than in NaOH (Wang et al. 2017). The formation of DES type of a complex between TEAOH and urea might have a similar effect. On the contrary, hydrogen bonding might also be one cause for the inability of a solution containing high carbamide content to dissolve

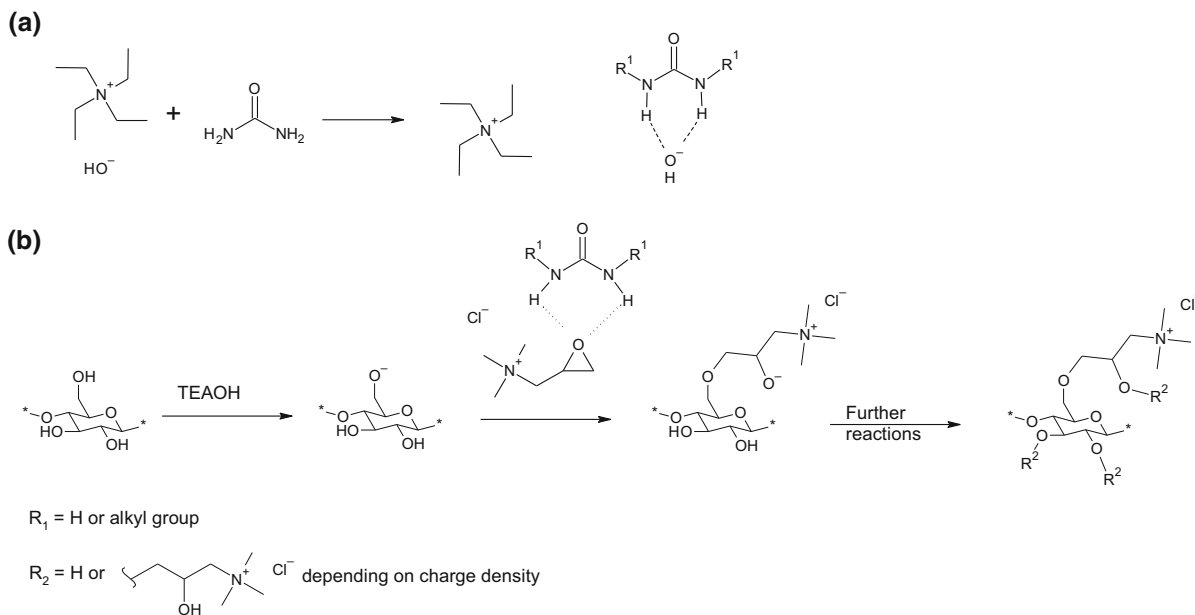
cellulose, as carbamides might act as a competing hydrogen bond donor for the hydroxide ion. When cellulose concentration is increased, at high carbamide content, there is less free hydroxide ions to interact with cellulose and therefore diminished dissolution.

It should be noted that the cation also has an effect on the formation of DESs. Previous studies have shown that although some sodium (and other alkaline) salts can form DESs (Abbott et al. 2016), they are rare, and many DESs are formed using organic cations. In the current study, it was observed that no clear liquid could be produced when 35 wt% NaOH solution in water was mixed with urea at a molar ratio of 1:2 of NaOH and urea. This indicates that the formation of a clear liquid with urea and TEAOH is not simple dissolution of urea in alkaline conditions. In contrast, clear liquid was formed by mixing 35% TEACl solution in water with urea at a molar ratio of 1:2. However, this solvent was unable to dissolve cellulose at room temperature. The inability of TEACl–urea solution to dissolve cellulose is similar to the comparison of the interaction of NaOH and NaCl with cellobiose, (Bialik et al. 2016) indicating the requisite of a certain level of basicity in the solvent for the dissolution of cellulose.

An important point regarding the formation of DES between TEAOH and carbamides is the presence of a substantial amount of water. At low water content, it has been proposed that water can take part in the formation of DES, and many DESs are formed using hydrates. However, when the amount of water is increased, the structure of DES is disintegrated and an aqueous solution of DES components is obtained (Hammond et al. 2017). With choline chloride–urea DES, the critical water content has been proved to be around 50%, similar to the highest water content studied here (Table 1). In addition, NaOH is known to form a eutectic mixture with water (Egal et al. 2007).

#### Homogenous cationization of cellulose

Aqueous alkaline solvents are studied for several chemical modifications of cellulose (Yan et al. 2009; Schmidt et al. 2014; Hu et al. 2015). Here, epoxide ring opening etherification with GTAC to produce cationic cellulose (Fig. 8b) was investigated in different TEAOH–carbamate solvents and the results are presented in Table 2. It should be noted that addition of GTAC into cellulose introduced additional



**Fig. 8** **a** Possible formation mechanism of deep eutectic system via hydrogen bond interaction between carbamide and the hydroxide ion of TEAOH (water and additional urea molecules

were omitted in sake of clarity), and **b** deprotonation of cellulose by TEAOH and reaction with carbamide activated GTAC to produce cationic cellulose

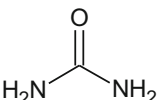
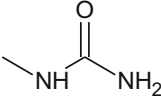
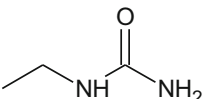
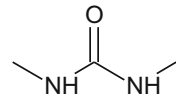
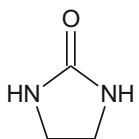
hydroxyl group, which in turn can react, the calculation of DS can be misleading (i.e. more than three GTAC groups can be introduced to one repeating unit of cellulose). Therefore, results are presented only as charge density. It can be seen that all of the studied novel solvents produced cationic cellulose with a higher charge density compared to aqueous NaOH (7 wt%) and urea (12 wt%) used as references. One possible explanation could be the homogeneity of the reaction solution. When GTAC was added to the cellulose solution in NaOH–urea, the solution became cloudy and remained as turbid suspension during the whole reaction time. The precipitation of cellulose has previously been reported during the cationization of cellulose in NaOH–urea with GTAC (Yan et al. 2009) and (3-chloro-2-hydroxypropyl)trimethylammonium chloride (GTAC precursor) (Li et al. 2015). However, previous studies reported the dissolution of the precipitated cellulose after stirring and the solution remained clear during the whole reaction time. A different behavior of cellulose in the present study compared to the previous study might be due to the difference in cellulose concentration: here, 5 wt% cellulose solution was used, whereas in the previous study, 3 (Li et al. 2015) and 2 (Yan et al. 2009) wt% cellulose solutions were used. Compared to NaOH–

urea solution, all the urea-containing TEAOH–carbamide–MCC solutions remained clear during the whole reaction time. In the case of MU, a gel-like material was obtained after the addition of GTAC; however, the reaction mixture became more liquid-like after some mixing.

Of all the carbamides used, the highest cationic charge was obtained using 1,3-DMU with a molar ratio of 1:2. The charge density obtained with this solvent was more than two times than that obtained with NaOH–urea. However, when the amount of 1,3-DMU was increased, the charge density decreased. In the case of 1,3-DMU with molar ratio of 1:3 and higher, it was observed that a gel-like material was obtained after the addition of GTAC, and at a molar ratio of 1:6 of TEAOH and 1,3-DMU, a stiff gel was formed, which could not be mixed anymore. However, all of the 1,3-DMU systems still produced cationic cellulose with a higher charge compared to the reference solvent.

The higher cationicity obtained with TEAOH–carbamide solutions compared to NaOH–urea solution might originate from higher concentration of hydroxyl ions and carbamides. High alkalinity results in deprotonation of cellulose, leading to the increase in nucleophilicity of hydroxyl groups, and thus improved

**Table 2** Charge densities of the cationic cellulose produced using carbamides at various carbamide–TEAOH molar ratios and the appearance of the reaction mixture during the reaction

Carbamide	Moles of carbamide per mol of TEAOH	Charge density (meq/g)	Appearance of reaction mixture
 Urea	2	1.8 ± 0.01	Clear liquid
	3	1.9 ± 0.02	Clear liquid
	4	2.1 ± 0.01	Clear liquid
	5	2.4 ± 0.04	Clear liquid
	6	2.1 ± 0.05	Clear liquid
	2	2.5 ± 0.01	Gel-like at the beginning; easy mixing
 Methylurea	3	2.7 ± 0.01	Gel-like at the beginning; easy mixing
	4	2.7 ± 0.00	Gel-like at the beginning; easy mixing
	5	2.1 ± 0.02	Gel-like at the beginning; easy mixing
	6	2.2 ± 0.01	Gel-like at the beginning; easy mixing
	7	2.1 ± 0.01	Gel-like at the beginning; poor mixing
	2	2.4 ± 0.00	Clear liquid
	 Ethylurea	2	3.0 ± 0.04
3		2.5 ± 0.04	Clear liquid
 1,3-Dimethylurea	4	2.0 ± 0.00	Gel-like at the beginning; easy mixing
	5	1.8 ± 0.00	Gel-like; poor mixing
	6	1.7 ± 0.00	Gel; hard to mix
	2	2.0 ± 0.02	Clear liquid
	 Imidazolidone	–	1.1 ± 0.04

Aqueous NaOH (7 wt%) and urea (12 wt%) were used as references. Reaction conditions included a molar ratio of 1:3 of MCC and GTAC, room temperature, 24 h, 5 wt% MCC concentration

<sup>a</sup>Reference solvent: Aqueous NaOH (7 wt%) and urea (12 wt%)

reactivity towards the epoxide ring. In addition, carbamide groups can activate epoxide groups by hydrogen bonding interaction (Fig. 8b), resulting in higher reactivity of epoxide groups towards nucleophilic components (Azhdari Tehrani et al. 2015; Liu et al. 2016). Due to the decreased solubility of cationic cellulose in some of the studied solutions (seen as formation of gel-like reaction mixture), no direct conclusion can be drawn from the reactivity of cellulose in solutions of different carbamides. However, it appears that introduction of electron donating groups (e.g. methyl and ethyl groups) in nitrogen

group can improve the catalytic activity of carbamide. The effect of electron donating group is evident from the fact that amount of urea has to be increased to 42 wt% to obtain similar cationic charge compared to, for example, cationic charge produced by solvent containing only 26 wt% of methylurea.

## Conclusions

It was shown here that other carbamides, instead of urea, can also be used to improve the dissolution of



cellulose in an aqueous alkaline solution. The dissolution efficiency depended on the structure of the carbamide, as, for example, two dimethylurea isomers had a completely different behavior: up to 56% 1,3-DMU-containing solvent (with a molar ratio of 1:5 of TEAOH and DMU) was able to dissolve 5% of cellulose, whereas no clear solvent could be produced when 1,1-DMU was mixed with TEAOH. The different behavior of two dimethylurea isomers indicated that the hydrogen in both amide nitrogens was important for the formation of an efficient solvent between carbamide and TEAOH, and the formation of DES type of a mixture was proposed. The highest amount (15%) of cellulose could be dissolved in TEAOH solution containing 22 wt% urea. All of the dissolution experiments were done at room temperature within 1 h, indicating that the studied solvent systems could be used in the production of bulk cellulose materials, such as films and fibers. Furthermore, it has been demonstrated that the carbamide-based solvent could be recycled and directly reused for the dissolution of cellulose. However, further studies are requested to fully understand the dissolution mechanism and long-term recyclability of solvents. Additionally, the use of TEAOH–carbamide solvents was demonstrated in the chemical modification of cellulose. Highly charged cationic cellulose could be obtained and a maximum reaction efficiency was observed when 1,3-DMU was used. All of the studied TEAOH–carbamide solutions showed higher reactivity compared to aqueous NaOH–urea solution.

**Acknowledgments** Open access funding provided by University of Oulu including Oulu University Hospital. J. A. S. thanks Kone Foundation for its financial support. Authors acknowledge Elisa Wirkkala for the elemental analysis and limiting viscosity measurements.

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