TEXAS TECH UNIVERSITY
Libraries™

SWITCHABLE CARBAMATE COAGULANTS TO IMPROVE RECYCLING IONIC LIQUID FROM BIOMASS SOLUTIONS

Green Chemical Engineering 2 (2021) 384–391

Contents lists available at ScienceDirect

Green Chemical Engineering

journal homepage: www.keaipublishing.com/en/journals/green-chemical-engineering

Article

Switchable carbamate coagulants to improve recycling ionic liquid from biomass solutions

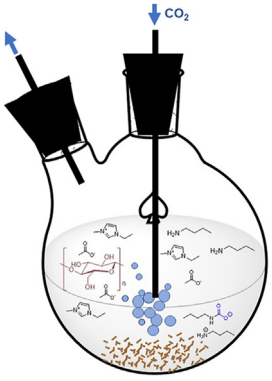
Julia L. Shamshina [a,*], Ying Qin [b], Ken Belmore [c], Daniel T. Daly [b], Robin D. Rogers [d,e,*]

[a] Fiber and Biopolymer Research Institute, Department of Plant and Soil Science, Texas Tech University, Lubbock, TX, 79409, USA
[b] Alabama Institute for Manufacturing Excellence, The University of Alabama, Tuscaloosa, AL, 35487, USA
[c] Department of Chemistry and Biochemistry, The University of Alabama, Tuscaloosa, AL, 35487, USA
[d] College of Arts & Sciences, The University of Alabama, Tuscaloosa, AL, 35487, USA
[e] 525 Solutions, Inc., P.O. Box 2206, Tuscaloosa, AL, 35403, USA

HIGHLIGHTS

- A methodology was developed to recover biopolymers in IL solution by changing solubility with reversible carbamate salts.
- The process can lower the energy usage in the recycling of ILs by lowering the amount of antisolvent to be removed.
- Cellulose and chitin were coagulated from [C_2mim][OAc] using triethanolamine, ethylenediamine, and butylamine carbamates.
- Cellulose fibers were extruded from [C_2mim][OAc] solution into a coagulating bath of butylamine carbamate.
- This work provides new directions in the search for more economically viable IL recycling processes in biomass treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Carbamate
Ionic liquid
Recovery
Switchable
Coagulation
Biopolymers
Carbamates
IL recycle

ABSTRACT

A reversible amine-carbamate approach has been developed to reduce the use of antisolvents such as water in the coagulation of biopolymers from ionic liquid (IL) solution and thus improve the economy of IL recycle. Cellulose and chitin were recovered from 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) solution by introducing the miscible amines triethanolamine (TEA), ethylenediamine (EDA), or butylamine (BA) and bubbling CO_2 at 40 °C and atmospheric pressure through the solutions to form carbamate salts *in situ* which resulted in biopolymer coagulation. BA gave the best results because of its low boiling point and low viscosity, which benefited both biopolymer recovery and IL recycle. Cellulose films and fibers could be formed by extrusion of an MCC/[C_2mim]-[OAc] solution into a coagulating bath comprised of a 1:1 M mixture of [C_2mim][OAc] and butylammonium butylcarbamate (BA-carbamate). The cellulose, IL, amine, and CO_2 were easily separated, although the cellulose recovered required some water washings to remove traces of IL. Up to 96.4% of the [C_2mim][OAc] could be recovered, 76.2% from the coagulation bath and 20.2% from the water washings. The recycled IL was suitable for another cycle of cellulose dissolution and extrusion and 84.6% of the IL used for the second cycle was recovered.

* Corresponding authors.
E-mail addresses: jshamshi@ttu.edu (J.L. Shamshina), robin.rogers@525solutions.com (R.D. Rogers).

https://doi.org/10.1016/j.gce.2021.07.001
Received 7 May 2021; Received in revised form 18 June 2021; Accepted 7 July 2021
Available online 12 July 2021

Although further work is needed, not the least of which will be reducing the amount of water needed for washing steps, some promising features of this process point the way for new directions for more economically viable IL recycling processes in biomass treatment with ILs.

1. Introduction

Ionic liquids (ILs, salts that melt at or below 100 °C [1]) have been found to be excellent and highly selective solvents for various biopolymers such as cellulose [2,3], chitin [4], and even wood [5]. While the technical achievements have been promising for the development of more sustainable materials from biopolymers, economic success seems to still hinge on cost effective recycling of the IL. ILs usually have low vapor pressure as a result of the strong ionic interaction between the constituent ions, a property which is favorable since they do not emit potentially hazardous vapors during operations and handling, but which makes it more difficult to recycle them since they cannot in general be distilled.

The general process for preparing a biopolymer material using an IL, includes first dissolution in the IL, then coagulating it in a specific architecture using an antisolvent (*e.g.*, water, ethanol, etc.) to wash out the IL and allow the hydrogen bonding and chain entanglement of the biopolymers to form solid constructs [4,6–15].Recovery of hydrophilic ILs from aqueous solution is generally not a technical challenge, but rather an economic one. The most common approach is to simply evaporate water, a highly energy intensive and generally more difficult process than separation of water from hydrophobic ILs [16]. However, the direct evaporation process is not only energy-consuming, with much of the energy penalty attributed to boiling water during the IL regeneration, occurring at > 100 °C; but also, if the IL to be recovered is thermodynamically unstable, such a process should be avoided or minimized. Thus, there is still a need for the development, engineering, and optimization of a process that can efficiently deliver, transfer, and recover the IL.

We wondered if a 'switchable' coagulant [17–19], one comprised of volatile components, could be used to recover the biopolymers from IL solution and then be easily removed from the IL. Aqueous amines, such as monoethanolamine (MEA) and diethanolamine (DEA), are used at scale in industry for CO_2 capture from natural gas extraction, gas refinery and exhaust gases due to high CO_2 absorption efficiency and loading capacity [20–23]. These reactions of amines with CO_2 have been extensively studied, particularly recently in the field of CO_2-capture and storage [24–26].

The reversible amine to carbamate transition results in a significant change from non-ionic amine to ionic carbamate upon reaction with CO_2, which can be employed not only in formation of switchable solvents and reversible ILs [27], but also *in solutions* with ions comprising ILs. This was demonstrated by Bara and coworkers [28,29] who found that MEA was soluble in certain imidazolium ILs and applied these systems for reversible capture of CO_2. IL/MEA solutions were able to rapidly reduce the concentration of CO_2 in a feed gas to concentrations of parts per million (ppm). In one example, a 1:1 (molar) 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_6mim][Tf_2N])/MEA mixture was capable of rapid and reversible capture of 0.5 mol of CO_2. These IL-amine solutions offered great benefits over conventional *aqueous* amine solutions, especially considering the energy requirement for water removal. This effectively launched the concept of using ILs *in a mixture* with amines for CO_2-capture [30–32]. The CO_2 capture occurs by formation of an insoluble MEA-carbamate, 2-hydroxyethylammonium (2-hydroxyethyl)carbamate (Scheme 1), and its precipitation drives the equilibrium of the CO_2-capture reaction forward. The release of captured CO_2 from the carbamate was achieved by either heating and/or reduced pressure.

We hypothesized that we could use this same approach to coagulate biopolymers in IL solution by formation of a carbamate salt where the strong hydrogen bond donors and acceptors of the carbamate salt would disrupt the hydrogen bonding between the biopolymer and the IL anion responsible for solution behavior, resulting in coagulation. If the biopolymer was also insoluble in the carbamate, the coagulation in this system would allow easy removal of the biopolymer, after which subjecting the carbamate to elevated temperature and reduced pressure would facilitate recovery of the IL that could easily be reused. Such an IL recycle process would avoid using the commonly used antisolvent water, thus saving energy and cost from evaporating the water [33].

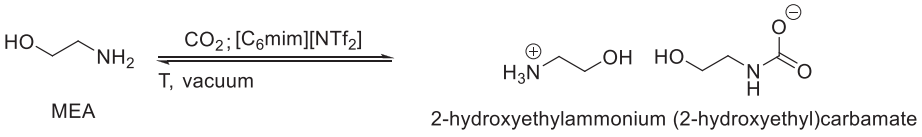
Aqueous alkanolamine solutions are frequently used as absorbents for removal of acidic gases (*e.g.*, CO_2 and H_2S) in industry [34], and the amines that have proved to be of principal commercial interest are MEA, DEA, and triethanolamine (TEA). In general, the hydroxyl group serves to increase the water solubility, while the amine group provides the necessary alkalinity in water solutions to cause the absorption of acidic gases [35]. Here, we describe our efforts to test our hypothesis by using these reversible carbamate systems to coagulate dissolved biomass and exemplify how this might be used in the production of cellulose or chitin films and fibers.

2. Experimental

2.1. Chemicals and materials

1-Ethyl-3-methylimidazolium chloride ([C_2mim]Cl) and 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) (purity ≥ 90%) were obtained from BASF (Ludwigshafen, Germany), and 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) (purity > 95%) was obtained from Iolitec (Tuscaloosa, AL) and used as received. Monoethanolamine (MEA), diethanolamine (DEA), butylamine (BA), and ethylenediamine (EDA) were purchased from Sigma-Aldrich (St. Louis, MO). Triethanolamine (TEA) was manufactured by Honeywell Riedel-De Haën (Seelze, Germany), supplied by Fischer Scientific (Hampton, NH) and used as received. Compressed CO_2 was purchased from Airgas (Tuscaloosa, AL). Microcrystalline cellulose (MCC) and practical grade chitin (PG-chitin) were purchased from Sigma-Aldrich (St. Louis, MO) and used directly without further purification. Deionized water (DI H_2O) was obtained from a commercial deionizer (Culligan, Northbrook, IL) with specific resistivity of 17.25 MΩ cm at 25 °C.

Synthesis of Ethylenediamine-Carbamate (EDA-carbamate). EDA (5 g, 83.1 mmol) was placed into a 20 mL glass vial, and heated to 40 °C. Gaseous CO_2 was bubbled into the amine solution with a flow rate of 70 cm^3 min^{-1} at 1 atm for 1 h. The EDA-carbamate formed was a white solid, and characterized with no additional purification. Ethylenediamine carbamate [$(NH_3CH_2)_2$][$(CH_2NHCOO)_2$]) was characterized by 1D (^{1}H, ^{13}C) and 2D (COSY, HSQC, and HMBC) NMR (D_2O) which



Scheme 1. Formation of 2-hydroxyethylammonium (2-hydroxyethyl)carbamate (MEA-carbamate).

confirmed the formulation to be bis(2-aminoethan-1-aminium) ethane-1,2-diyldicarbamate and 2-aminoethan-1-aminium(2-aminoethyl)carbamate in a 0.4:1 ratio. ^{1}H NMR (D_2O): δ 4.8 (s, 8H, 2 × (NH_3 + NH), exchange), 3.1 (t, 4H, 2 × CH_2), 2.77 (t, 4H, 2 × CH_2). δ 164.8 (COO^-), 41.6 (CH_2), 40.3 (CH_2), 40.7 (CH_2), 40.9 (CH_2). Correlated Spectroscopy (COSY), Heteronuclear Single-Quantum Correlation (HSQC) and Heteronuclear Multiple-Bond Correlation (HMBC) spectra are available in the SI (Figs. S9–S13).

Synthesis of Butylamine-Carbamate (BA-carbamate). Colorless butylamine (BA) (10 g, 136.7 mmol) were placed into a 20 mL glass vial, and heated to 40 °C. Gaseous CO_2 was bubbled into the amine solution with a flow rate of 70 cm^3 min^{-1} at 1 atm for 1 h. The butylcarbamate formed was a white solid and characterized with no additional purification. The formulation, butylammonium butylcarbamate ([$C_4H_9NH_3$]-[$C_4H_9NH_2COO$]) was confirmed by 1D (^{1}H, ^{13}C) and 2D (COSY, HSQC, and HMBC) NMR (D_2O). ^{1}H NMR (D_2O): δ 2.90 (t, 2H, CH_2), 2.84 (t, 2H, CH_2), 1.51 (quintet, 2H, CH_2), 1.32 (quintet, 2H, CH_2), 1.29 (sextet, 2H, CH_2), 1.21 (sextet, 2H, CH_2), 0.83 (t, 3H, CH_3), 0.80 (t, 3H, CH_3); ^{13}C NMR (D_2O): δ 164.77 (COO^-), 40.96 (CH_2), 39.24 (CH_2), 31.73 (CH_2), 29.37 (CH_2), 19.37 (CH_2), 18.98 (CH_2), 13.13 (CH_3), 12.77 (CH_3). COSY, HSQC, and HMBC spectra are provided in the SI (Figs. S9–S11).

2.2. Dissolution and coagulation of biopolymers

MCC/[C_4mim]Cl/TEA. MCC (0.2 g, 3.85 wt% with respect to the IL) was added to [C_4mim]Cl (5.00 g, 28.6 mmol) pre-heated slightly above its melting point (~70 °C) and then heated to 100 °C and stirred at this temperature for 10 min, to obtain a clear solution of MCC (3.85 wt%). TEA (4.27 g, 28.6 mmol) was added to the solution at room temperature, resulting in gelation upon stirring after 2 min. The gel was liquefied by slowly heating the mixture to 90 °C over 3 h; then the solution was cooled to 40 °C. Gaseous CO_2 was bubbled into the solution of MCC in [C_4mim]Cl/TEA with a flow rate of 70 cm^3 min^{-1}, at 40 °C under atmospheric pressure for 24 h, until the MCC had completely precipitated. The mixture was then subjected to vacuum filtration, and due to the high viscosity of the mixture, the separation funnel and filtration flask were kept warm in an oven (Fisher Scientific Isotemp 285 A Vacuum Oven, Fischer Scientific, Portsmouth, NH), at 50 °C. Upon filtration, a light yellowish gel formed on the top of the filter paper which was separated from a bright yellow supernatant. The gel then solidified while being washed with ~20 mL DI H_2O giving a white solid. After that, the filtration flask was replaced with a new one, and the separated solid was further washed with 50 mL DI water after vacuum filtration, dried, and weighed. *Note:* The addition of water at this stage (here and in subsequent examples) was only for analytical purposes, that is to remove the small residual of IL or carbamate left on the solid so it could be weighed for mass balance.

In a separate experiment, an equimolar [C_4mim]Cl/TEA solution was prepared by mixing [C_4mim]Cl (0.756 g, 4.3 mmol) and TEA (4.3 mmol, 0.644 g) at room temperature (RT), followed by addition of MCC (0.0076 g, 0.99 wt% with respect to the IL), heating to 90 °C and stirring at this temperature for 3 days. The MCC was not dissolved under these conditions. Increasing the relative amount of the IL to 2:1 [C_4mim]Cl/TEA, prepared by mixing of 5 g (28.6 mmol) [C_4mim]Cl and 2.135 g (14.3 mmol) TEA at RT, was insufficient to dissolve 0.05 g MCC even after heating to 90 °C and stirring at this temperature for 2 days. Increasing the amount of IL amount to 4:1 [C_4mim]Cl/TEA, also did not result in MCC dissolution under the same conditions.

MCC/[C_2mim][OAc]/TEA. MCC (0.1 g, 1.96 wt% with respect to the IL) was added to [C_2mim][OAc] (5.00 g, 29.4 mmol) and then heated to 120 °C and stirred at this temperature for 20 min, to obtain a clear solution of MCC (1.96 wt%). TEA (2.97 g, 29.4 mmol) was added to the solution at room temperature, resulting in phase separation. Under intensive stirring of the biphasic solution, gaseous CO_2 was bubbled into the mixture with a flow rate of 70 cm^3 min^{-1}, at 40 °C under atmospheric pressure for 10 min, and despite the immiscibility of phases, some precipitate was formed. We did not attempt to isolate the precipitate in this case, as the amount of precipitate was low.

MCC/[C_4mim]Cl/EDA. MCC (0.1 g, 1.96 wt% with respect to the IL) was added to [C_4mim]Cl (5.00 g, 28.6 mmol) pre-heated slightly above its melting point (~70 °C) and then heated to 100 °C and stirred at this temperature for 10 min, to obtain a clear solution of MCC. EDA (1.72 g, 28.6 mmol) was added to the solution at room temperature, resulting in a clear yellow solution. Gaseous CO_2 was bubbled into the solution with a flow rate of 70 cm^3 min^{-1}, at 40 °C under atmospheric pressure for 22 h, with formation of a clear yellow gel, but no precipitate. The gel was not suitable for the separation.

In a separate experiment, MCC (0.0152 g, 1.97 wt% with respect to the IL) was added to 1.21 g of an equimolar [C_4mim]Cl/DEA solution (prepared by mixing [C_4mim]Cl (0.756 g, 4.3 mmol) and DEA (0.452 g, 4.3 mmol) at RT) followed by heating to 90 °C, with stirring for 2 days. MCC did not dissolve under these conditions.

PG-chitin/[C_2mim][OAc]/EDA. Practical grade (PG)-chitin, 0.050 g (0.99 wt% with respect to the IL) was stirred with [C_2mim][OAc] (5.00 g, 29.4 mmol) at 130 °C for 30 min to obtain a clear solution. After cooling to RT, EDA (1.77 g, 29.4 mmol) was added and the solution stirred for 2 min. The solution was then heated to 40 °C with stirring, and gaseous CO_2 was bubbled through the solution with a flow rate of 70 cm^3 min^{-1} at 1 atm for 24 h after which the chitin had completely precipitated. The precipitate was then separated from the solution by means of vacuum filtration to give a yellowish solid and bright yellowish liquid. After that, the filtration flask was replaced with a new one, and the separated slightly yellow solid was further washed with 50 mL DI water after vacuum filtration, dried, and weighed.

The same reaction was also conducted with 1.96 wt% (0.100 g) PG-chitin and the chitin dissolved after 1.5 h. The CO_2 bubbling and separation proceeded as previously described.

In an alternative strategy, PG-chitin, 0.1 g (1.96 wt%) was stirred with [C_2mim][OAc] (5 g, 29.4 mmol) at 120 °C for 2 h to obtain a clear solution. EDA-carbamate (6.122 g, 29.4 mmol)) was added and the solution heated to 40 °C with stirring for 2 days which resulted in formation of a very viscous gel, with no crystalline precipitate.

MCC/[C_2mim][OAc]/EDA([C_2mim][OAc]:EDA = 1:1, 2:1, 3:1, 4:1, 6:1, and 8:1). Equimolar amounts of [C_2mim][OAc] (10 g, 58.7 mmol) and EDA (3.53 g, 58.7 mmol) were mixed at room temperature to obtain a homogeneous mixture. MCC (0.4 g, 3.85 wt% with respect to the IL) was added and the suspension was heated with stirring to 90 °C and held for 30 min until the MCC was completely dissolved. The solution was then cooled to 40 °C, and gaseous CO_2 was bubbled into the solution with a flow rate of 70 cm^3 min^{-1} and 1 atm for 24 h after which the mixture was solid (precipitate started forming after 2 h of CO_2 bubbling). The solid carbamate was melted upon heating in an oven at 70–80 °C and the yellowish MCC and bright yellowish liquid were then separated from the solution by means of vacuum filtration as described above. After collecting supernatant, and switching the filtration flask, the precipitate was additionally washed with 50 mL DI water as also noted above giving a white solid which was dried and weighed.

Additional [C_2mim][OAc]/EDA solutions were prepared as above in [C_2mim][OAc]:EDA ratios of 2:1, 3:1, 4:1, 6:1, and 8:1. MCC was added to each solution at 1.96 wt% with respect to the IL, and the suspensions were heated with stirring to dissolve the MCC. Each solution was then cooled to 40 °C, and gaseous CO_2 was bubbled into the solution with a flow rate of 70 cm^3 min^{-1} and 1 atm for 24 h. The specifics for each solution are noted below.

2:1 [C_2mim][OAc]:EDA [C_2mim][OAc] (10 g, 58.7 mmol), EDA (1.765 g, 29.4 mmol), MCC (0.2 g, 1.96 wt% with respect to the IL), heating to 100 °C and held at 90 °C, for 15 min; upon CO_2 addition the mixture fully solidified in 4.5 h. *2:1 [C_2mim][OAc]:EDA* [C_2mim][OAc] (5 g, 29.3 mmol), EDA (0.588 g, 9.79 mmol), MCC (0.1 g, 1.96 wt% with respect to the IL), heating with stirring to 90 °C for 15 min; upon CO_2 addition the mixture fully solidified in 3.3 h.

4:1 [C_2mim][OAc]:EDA [C_2mim][OAc] (5 g, 29.4 mmol), EDA (0.444 g, 7.34 mmol), MCC (0.1 g, 2 wt% with respect to the IL), heating with

stirring to 90 °C for 15 min; upon CO_2 addition the mixture fully solidified in 3.0 h.

6:1 [C_2mim][OAc]:EDA [C_2mim][OAc] (8 g, 47.0 mmol), EDA (0.471 g, 7.83 mmol), MCC (0.16 g, 1.96 wt% with respect to the IL), heating with stirring to 90 °C for 15 min; upon CO_2 addition the mixture fully solidified in 5.0 h.

8:1 [C_2mim][OAc]:EDA [C_2mim][OAc] (8 g, 47.0 mmol), EDA (0.353 g, 5.88 mmol), MCC (0.16 g, 1.96 wt% with respect to the IL), heating with stirring to 90 °C for 15 min; upon CO_2 even after 19.6 h no traces of precipitate were observed.

MCC/[C_2mim][OAc]/BA. In 5 vials, MCC, 0.1 g (1.96 wt% with respect to the IL) was added to 5 g of [C_2mim][OAc] (29.4 mmol) and the mixtures heated with magnetic stirring to 100 °C, kept at this temperature for 30 min to obtain a clear solution, and cooled to RT. BA was added in different amounts to each vial and stirred for 2 min: 29.4 mmol (2.485 g, IL:BA = 1:1) in two of the vials, 1.433 g (19.6 mmol, IL:BA = 1:0.66), 1.229 g (16.8 mmol, IL:BA = 1:0.57), and 1.243 g (14.7 mmol, IL:BA = 1:0.5). After heating to 40 °C with stirring, gaseous CO_2 was bubbled into the solutions at a flow rate of 70 cm^3 min^{-1} and 1 atm for up to 24 h to precipitation the MCC. There was no precipitate formed from solutions of IL:BA of 1:0.57 or 1:0.5, while all other solutions did give MCC precipitate. The precipitate which formed from the remaining solutions was then separated by means of vacuum filtration giving yellowish solids and bright yellowish liquids. Switching to a new filtration flask and washing the solids with additional water gave yellowish solids that were dried and weighed.

2.3. Preparation of films and fibers from biopolymers

*Coagulation Bath*1 BA-*carbamate Dissolved in IL*: A coagulating bath was prepared by mixing with stirring 17 g of [C_2mim][OAc] (100 mmol) with 15 g (127 mmol) of BA-carbamate for 30 min at RT.

*Coagulation Bath*2 BA-*carbamate Formed in situ*: A coagulating bath was prepared by mixing 17.1 g of [C_2mim][OAc] (100 mmol) with 11.4 g (100 mmol) of BA at RT with stirring for 30 min. The solution was heated to 40 °C and CO_2 was bubbled through the solution at a flow rate of 70 cm^3 min^{-1} at 1 atm for 24 h.

MCC Fibers Prepared from MCC/[C_2mim][OAc]/BA. MCC was suspended in 5 g of [C_2mim][OAc] and heated to 100 °C for 10 min to obtain a clear solutions of MCC at the following concentrations: 3.85 wt% (0.2 g MCC/5 g IL), 7.4 wt% MCC (0.4 g MCC/5 g IL), 9.0 wt% MCC (0.5 g MCC/5 g IL), 10.7 wt% MCC (0.6 g MCC/5 g IL), and 15.2 wt% MCC (0.9 g MCC/5 g IL). BA-carbamate, 25 g, was placed into 35 g of [C_2mim]-[OAc] and stirred at RT for 24 h to form a clear solution.

The MCC/IL solution was degassed in an oven (Fisher Scientific Isotemp 285 A Vacuum Oven, Fischer Scientific, Portsmouth, NH) for 15 min and carefully loaded into a 10 mL syringe which was then mounted onto a syringe pump (Model No. NE-1010, New Era Pump Systems, Inc, Farmingdale, NY). A heating sleeve was wrapped around the syringe, heated, and kept at 68 °C, for the duration of extrusion. Fibers were extruded at a rate 1 mm min^{-1} into a plastic Petri dish (8.5 cm diameter × 1.2 cm deep) containing the IL/BA-carbamate solution. No fiber was formed using solutions containing 3.85, 7.4, 9.0, or 10.7 wt% MCC, but instead the MCC coagulated as a film at the bottom of the Petri dish. Rudimentary fibers did form upon extrusion of the 15.2 wt% MCC/IL solution. The resultant fibers were soaked in BA-carbamate/IL solution for 5–24 h, and then transferred into 50 mL DI H_2O and kept there for a day to remove any residual IL. The fibers were then air-dried.

MCC Films Prepared from MCC/[C_2mim][OAc]/BA. MCC (0.8 g or 0.9 g) was suspended in 5 g of [C_2mim][OAc] and heated to 100 °C for 10–75 min to obtain clear solutions of 10.7, 13.0, or 15.2 wt%, respectively. BA-carbamate, 17 g, was placed into 15 g of [C_2mim][OAc] and stirred at RT for 24 h to form a clear solution. The MCC/IL solution was cooled to ~65 °C carefully cast onto a glass plate using a roller, and placed into a plastic Petri dish (8.5 cm diameter × 1.2 cm deep). The BA-carbamate/IL solution was slowly poured onto the cast area, and left for 6 h. After that time the film which had formed was transferred into 50 mL DI H_2O and kept there for a day to remove any residual IL. The film was then air-dried.

2.4. IL recovery

IL Recovery after Precipitation of MCC or Chitin. To determine the total amount of IL which could be recovered from the filtration and washing steps, the washings were combined and heated in an oil bath at 110 °C for 1 h to evaporate the water. The residue was combined with the supernatant separated during vacuum filtration. After evaporation using rotary evaporation, the residue was further dried in a vacuum oven (Fisher Scientific Isotemp 285 A Vacuum Oven, Fischer Scientific, NH) at 80 °C and vacuum of −30 inches Hg for 3 h.

IL Recovery after Formation of Fibers or Films. After removal of the fiber or film, the [C_2mim][OAc]/BA-carbamate coagulation bath was heated to 100 °C, and stirred for 1 h to decompose the carbamate into BA and CO_2 and evaporate both. The DI wash water was heated in an oil bath at 110 °C for 1–4 h to evaporate most of the water. The remaining IL and water washings residue were combined and further dried in a vacuum oven at 80 °C and −30 in Hg vacuum for 3 h until no bubbles could be observed.

Reusability of the Recycled IL. MCC (0.9 g) was suspended in 5 g of recycled [C_2mim][OAc] and heated to 120 °C for 0.66 h to obtain a clear solution of 15.2 wt%. It was noted that dissolution of MCC required a longer time and higher temperature than earlier. BA-carbamate, 8.66 g, was placed into 7.6 g of recycled [C_2mim][OAc] and stirred at RT for 24 h to form a clear solution. The MCC/IL solution was cooled to ~68 °C, loaded into a syringe, and the syringe covered by heating sleeve with a set temperature of 68 °C. The solution was extruded into IL/BA-carbamate solution as described earlier (rate 1 mL min^{-1}); to form fibers. The resultant fibers were soaked in BA-carbamate/IL solution for 6 h, and then transferred into 50 mL DI H_2O and kept there for a day to remove any residual IL. The fibers were then air-dried, and weighed; 0.82 g fibers (91.4%) were collected.

The DI H_2O washings were heated in an oil bath at 100 °C with stirring for 24 h to evaporate the water, and then the residue was further dried in a vacuum oven (Fisher Scientific Isotemp 285 A Vacuum Oven, Fischer Scientific, Portsmouth, NH) at 70 °C and vacuum of −30 inches Hg for another 3 h, to constitute the fraction "IL obtained from water washings of fibrous materials", 3.68 g or 29.2% of all IL (used for dissolution of MCC and dissolution of BA-carbamate). In parallel, [C_2mim][OAc]/BA-carbamate coagulation bath was heated with stirring to 90 °C for 3 h and then further dried in a vacuum oven (Fisher Scientific Isotemp 285 A Vacuum Oven, Fischer Scientific, NH) at 70 °C and vacuum of −30 inches Hg for another 3 h, to provide "IL obtained from a coagulation bath", 6.98 g (55.4%). Altogether this constituted 10.66 g of recovered IL after the second cycle (84.6% recovered IL).

The study of reusing the recycled IL after preparation of BA-carbamate *in situ* was conducted similarly with the exception that instead of placing BA-carbamate into the recycled [C_2mim][OAc] (7.6 g, 45 mmol), BA was added (3.32 g, 45 mmol), the mixture stirred, heated to 40 °C, and gaseous CO_2 was bubbled into the solution with a flow rate of 70 cm^3 min^{-1} and 1 atm for 24 h. The fiber pulling and IL recovery were then conducted as described above.

3. Results and discussion

3.1. Dissolution and coagulation testing

To test our hypothesis we chose to study two biopolymers, cellulose and practical grade (PG)-chitin, two ILs known to dissolve them, 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) and 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) [2,4], and three amines, triethanolamine (TEA), ethylenediamine (EDA), and butylamine (BA). The three amines are known to form carbamates as illustrated in Scheme 2.

We chose to approach the problem in two different ways. In the first approach we prepared solutions of the biopolymers in the IL, then dissolved in the amine, followed by bubbling CO_2 into the solution to form the carbamate and precipitate the biopolymer. In the second approach we prepared a solution of amine and IL first, then attempted to dissolve the biopolymer. A brief summary of our observations follow.

MCC/[C4mim]Cl/TEA. A 3.85 wt% solutions of MCC in [C4mim]Cl was prepared by adding the solid biopolymer to the IL, and then heating with stirring at 100 °C for a few minutes, to obtain a clear, yellowish solution which was cooled to RT. An equimolar amount of TEA relative to the IL was then added resulting in formation of a gel (Fig. 1, **Left**). The gel was liquefied by heating at 90 °C for 3 h, then cooled to 40 °C, and gaseous CO_2 was bubbled into the solution with a flow rate of 70 cm^3 min^{-1} for 24 h until the MCC had completely precipitated (Fig. 1, **Middle**).

Due to the high viscosity of the remaining solution, the solution was heated to 50 °C and vacuum filtration used to separate the yellowish solid from the yellowish liquid and release CO_2 (Fig. 1, **Right**). In order to quantify the solid by removing residual solvents, it was washed with a minimum amount of DI H_2O resulting in a white solid. FT-IR (SI, Figs. S1 and S2) confirmed the solid was MCC free of IL and the separated liquid was a mixture of [C4mim]Cl and TEA.

In order to manage the high viscosity and avoid the gel formation, we also attempted to use the reagents in different order, namely though mixing of equimolar amounts of [C4mim]Cl and TEA, followed by addition of 0.99 wt% MCC, but MCC did not dissolve even after prolonged (3 days) heating at 90 °C. Increasing the amount of IL to 2:1 or even 4:1 mol/mol [C4mim]Cl:TEA was not sufficient to dissolve MCC.

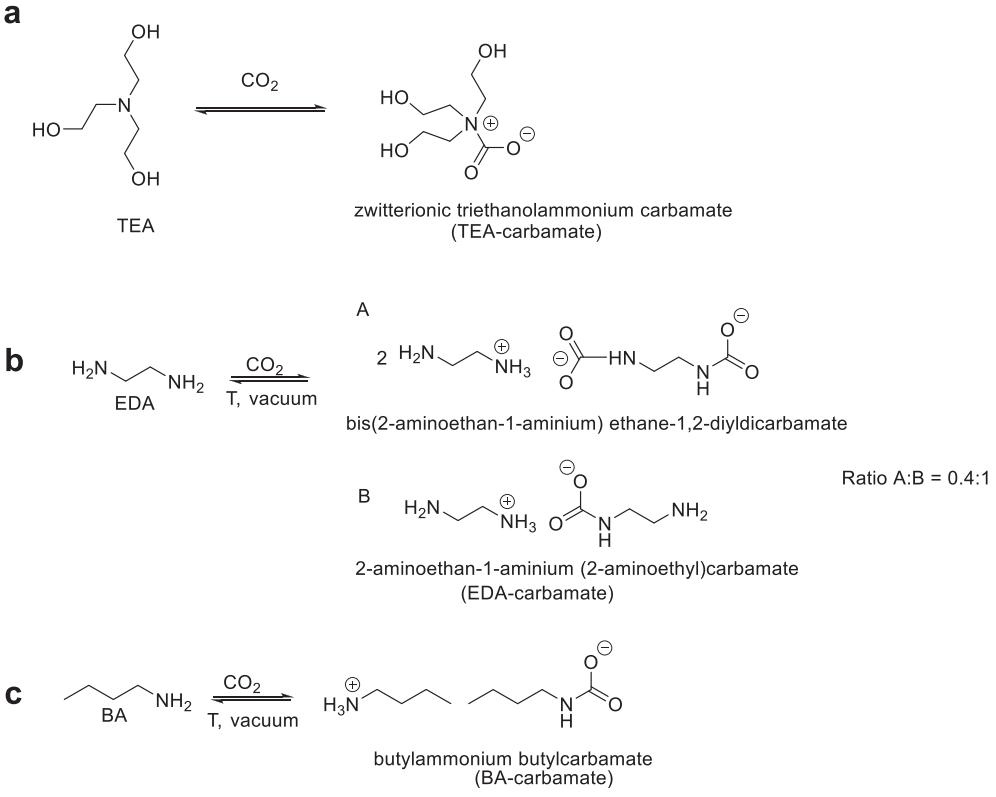
This experiment confirmed two of our assumptions. First, the formation of zwitterionic triethanolammonium carbamate (TEA-carbamate) according to Scheme 2a) decreases the solubility of MCC in the IL, presumably because new interactions between the carbamate salt and the IL compete with the hydrogen bonding between the Cl^- anion and the hydroxyl groups of MCC. In addition, the carbamate dissociates under vacuum, releasing free TEA and volatilizing the CO_2 [27].

Fig. 1. Left: clear gel formed after mixing TEA with the MCC/[C4mim]Cl solution at RT; Middle: solid precipitate upon bubbling CO_2 at 40 °C for 24 h; Right: solid MCC was obtained *via* vacuum filtration.

Since the amine might also have to be removed to recycle the IL, one may want to use amines of lower boiling point, and less substituted to be miscible with the IL. With this in mind, we switched our attention to primary amines with relatively low boiling points (*ca.* 75–120 °C), and turned our attention to ethylenediamine (EDA) (bp 118 °C).

MCC/[C4mim]Cl/EDA. MCC was thermally dissolved in [C4mim]Cl and EDA was added at RT, resulting in a homogeneous clear yellow solution. Gaseous CO_2 was bubbled into the solution at 40 °C with a flow rate of 70 cm^3 min^{-1} at 1 atm for 22 h, and a clear yellow gel formed, but without a precipitate. The gel appeared even more firm than we observed in the above work with MCC/[C4mim]Cl/TEA and was not suitable for the separation step. To overcome the RT gelation experienced with [C4mim]Cl, we then moved to examine the less viscous and more solubilizing IL, [C2mim][OAc] [4], and first proceeded with the same amines.

MCC/[C2mim][OAc]/TEA. MCC was thermally dissolved in [C2mim][OAc] and TEA was added to the solution at RT which resulted in phase separation. Under intensive stirring of the biphasic system, gaseous CO_2 was bubbled into the mixture at 40 °C with a flow rate of 70 cm^3 min^{-1} at 1 atm for 10 min. Despite the immiscibility of the phases, some precipitate was formed, however the amount of precipitate was too low to continue this experiment.



Scheme 2. Formation and decomposition of ammonium carbamates of (a) TEA, (b) EDA, and (c) BA.

MCC/[C$_2$mim][OAc]/EDA. In this experiment, EDA was first dissolved in the IL and then MCC was added. Using 10 g of the IL, equimolar amounts of [C$_2$mim][OAc] and EDA were mixed at RT, readily forming a solution. MCC (0.4 g, 3.85 wt% with respect to IL) was added, and the suspension was heated with stirring to 100 °C and mixed 30 min until the MCC was completely dissolved. Bubbling CO_2 into the solution (40 °C, 70 cm^3 min^{-1}, 1 atm, for 24 h) resulted in precipitation. Vacuum filtration was used to separate the yellowish solid from the yellowish liquid and in this case, the less viscous [C$_2$mim][OAc] did not present any difficulty. FT-IR (SI, Fig. S3) confirmed the solid was MCC free of IL and the separated liquid was a mixture of [C$_2$mim][OAc] with no residual EDA.

While testing other [C$_2$mim][OAc]:EDA molar ratios, we found that solubilized MCC could be precipitated upon carbamate formation when the ratio of [C$_2$mim][OAc]:EDA was 1:1 up to 6:1. When this ratio was above 6:1 MCC could not be precipitated. This finding suggests an optimized process could use much less EDA and this should improve the economics of the process.

PG-chitin/[C$_2$mim][OAc]/EDA. Based on the success with MCC, we also tested another biopolymer, practical grade (PG)-chitin, which is more difficult to dissolve than MCC. PG-chitin was thermally dissolved in 5 g of [C$_2$mim][OAc] to obtain a clear 0.99 wt% solution which was then cooled to RT. An equimolar amount (relative to the IL) of EDA was then added and the solution stirred at RT for 2 min without gelation. The solution was heated to 40 °C and CO_2 was bubbled through the solution (70 cm^3 min^{-1}, 1 atm, up to 24 h) to precipitate the chitin. The precipitate and supernatant were treated as above and FT-IR indicated the solid to be pure chitin and the liquid pure [C$_2$mim][OAc], with no traces of EDA or EDA-carbamate (SI, Fig. S4).

At this point we became interested whether addition of a preformed carbamate to the MCC/IL solution would also result in precipitation. This could be more cost-efficient because after bulk synthesis of carbamate (or commercial acquisition of such) we could eliminate the step of bubbling CO_2 into the solution.

To test this hypothesis, we prepared EDA-carbamate separately, by reaction with CO_2 at 40 °C for 1 h [36] 1D and 2D NMR analyses of the product (^{1}H, ^{13}C, HSQC, HMBC, HSQC, SI, Figs. S7–S11) confirmed the formation of 2-aminoethan-1-aminium (2-aminoethyl)carbamate (71%) slightly contaminated with a dicarbamate biproduct, bis(2-aminoethan-1-aminium) ethane-1,2-diyldicarbamate (Scheme 2b), EDA-carbamate). However, when a solution of 1.3 g PG-chitin in 5 g [C$_2$mim][OAc] (1.96 wt%) solution was mixed with equimolar amount of EDA-carbamate (6.122 g), a very viscous gel was formed, with no precipitate.

The most difficult part of this process was the separation of precipitated biopolymer from the IL and EDA-carbamate. The gel-like nature of the [C$_2$mim][OAc]/EDA-carbamate solution made the vacuum filtration process extremely slow, requiring the separation to be conducted warm either by putting it in an oven or by using a heat gun frequently. It was complicated by the fact that if the mixture was held at elevated temperature, the carbamate would decompose and the precipitated biomass would redissolve. Considering that EDA is also more chemically reactive due the existence of two active functional groups bringing added complexity, we decided to move to the use of primary amines with lower boiling points to both reduce the viscosity and facilitate the processing.

MCC/[C$_2$mim][OAc]/BA. In this experiment we chose to use the low boiling (bp = 78 °C) BA. MCC was added to [C$_2$mim][OAc] and thermally dissolved to provide a 4 wt% as noted above. The solution was then cooled to RT and BA was added and stirred at RT for 2 min. After heating to 40 °C, CO_2 was bubbled into the solution (70 cm^3 min^{-1}, 1 atm, 24 h) to precipitate the MCC. The separation of the solid and liquid was much easier for this system due to the much lower viscosity. The separated solids were worked up for analysis as noted above. FT-IR (Fig. S5) confirmed the MCC to be free of IL and amine. The recovered IL also had no amine residual.

To improve the economics of the process, we proceeded with determination of the minimum amount of BA necessary to be added. For this, we have synthesized BA-carbamate, by reaction with CO_2 at 40 °C for 1 h again, 1D and 2D NMR analyses of the product (^{1}H, ^{13}C, COSY, HSQC, HMBC, SI, Figs. S12–S16) confirmed the formation of butylamine carbamate (Scheme 2c), BA-carbamate, and repeated the same experiment noted above using ratios of [C$_2$mim][OAc]:BA = 1:0.67, 1:0.57, and 1:0.5). After gaseous CO_2 was bubbled into each solution (40 °C, 70 cm^3 min^{-1}, 1 atm, 24 h), it was found that the minimum amount of BA needed was 0.66 mol/mol of the IL.

3.2. Cellulosic fibers and films coagulated with carbamate

We have previously shown that cellulose dissolved in [C$_2$mim][OAc] can be extruded to produce fibers or cast to form films [4,6]. Typically this is done with water as the coagulant which leads to large volumes of aqueous IL for recycle. Since we were successful in coagulating cellulose from IL solution using the carbamate approach described above, we hypothesized that the carbamate could also act in a controlled manner allowing coagulation of cellulose as fibers or films.

To test this, we prepared [C$_2$mim][OAc]/BA-carbamate coagulating baths by two different methods. In the first method, BA-carbamate was dissolved in [C$_2$mim][OAc] in a 1:1 M ratio at RT and stirring for 30 min. In the second method, BA was dissolved in [C$_2$mim][OAc] in a 1:1 M ratio by stirring at RT and the resulting solution was heated to 40 °C followed by bubbling CO_2 through the solution at the conditions noted earlier.

Then 3.85, 7.4, 9.0, 10.7, and 15.2 wt% solutions of MCC in [C$_2$mim][OAc] were prepared and loaded into a 10 mL syringe which was wrapped with a heat tape and attached to a syringe pump. The solutions were heated to 67 °C and extruded into the RT coagulation bath made by the first method at a rate of 1 mL min^{-1}. Solutions of MCC below 15.2 wt% were of too low viscosity and failed to form fibers, but the MCC did coagulate in fragments which dropped to the bottom of the bath.

Rudimentary fibers were formed when extruding the 15.2 wt% solution into either of the two coagulation baths (Fig. 2). After 24 h, the fibers were pulled from the bath and soaked in DI H_2O to remove excess [C$_2$mim][OAc] and carbamate. When extruded into the pre-made BA-carbamate dissolved in IL, the dried fibers constituted 99.9% of the loaded MCC. However, when extruded into BA-carbamate formed *in situ*, MCC only 75.3% of the cellulose in the form of fibers and fibrous fragments were recovered; some cellulosic remnants were too small to be collected. This might be indicative of a smaller amount of BA-carbamate dissolved in the IL, due to insufficient time of CO_2 bubbling, which may not have completly converted BA into the carbamate. This experiment proves that while BA-carbamate could be formed *in situ*, it is more reliable to use pre-made carbamate, to ensure its proper concentration in the IL.

The same coagulation baths were also tested for casting films. We observed that films could be readily prepared from both the 10.7, and 15.2 wt% MCC/IL solutions. After the thermal dissolution of MCC in [C$_2$mim][OAc], the solutions were cooled to ~65 °C, and carefully cast onto a glass plate, which was then placed into a plastic Petri dish. Then

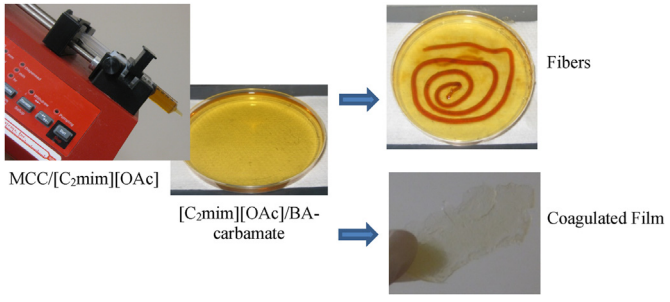


Fig. 2. An MCC fiber and film coagulated from [C$_2$mim][OAc] solution into [C$_2$mim][OAc]/BA-carbamate.

Table 1
Summary of recovery of IL and MCC from two consecutive cycles with two coagulating baths.

Coagulation bath		BA-carbamate dissolved in IL		BA-carbamate formed *in situ*	
		Cycle 1	Cycle 2	Cycle 1	Cycle 2
Recovered IL, %	IL obtained from coagulation bath	76.2	55.4	72.6	84.3
	IL obtained from water washings of fibrous materials or films	20.2	29.2	25.8	7.3
	Total recovered IL	**96.4**	**84.6**	**98.4**	**91.6**
Recovered MCC (fibers), %	Fibers prepared/ removed	99.9	91.4	64.5	66.1
	Pieces left in water washings	0	0	10.9	6.9
	Total recovered MCC	**99.9**	**91.4**	**75.4**	**73.1**

the coagulation bath solution was slowly poured onto the cast film, to cover it all, and left in a Petri dish undisturbed. The films were soaked in this manner in BA-carbamate/IL solution for 6 h, and then transferred into 50 mL DI H_2O and kept there for a day to remove any residual IL. The films were then air-dried (Fig. 2).

3.3. Ionic liquid recovery and reuse after fiber or film coagulation

The IL was recovered by heating the [C_2mim][OAc]/BA-carbamate coagulating baths (prepared by either method) at 100 °C to dissociate the carbamate and release both CO_2 and volatile amine. Any residual moisture or other volatiles were then removed by vacuum oven heating. Additional IL was recovered from the water washings, although this required evaporation of the water. NMR spectroscopy revealed the recovered IL to have no detectable water (SI, Fig. S17), even though water was detected by NMR in the IL as purchased from the supplier.

In our study of the coagulation bath prepared by dissolving BA-carbamate in the IL, we observed 76.2% of the IL could be recovered from the coagulation bath and 20.2% from the water washings for a total of 96.4% (Table 1), and its ^{1}H and ^{13}C spectra confirmed its purity (SI, Figs. S17 and S18). Repeating this experiment with the coagulation bath with the *in situ* generated BA-carbamate, we obtained similar recoveries of 72.6% from the coagulating bath and 25.8% from the water washings for a total recovery of 98.4%.

The reusability of the recycled IL was studied by dissolution of fresh MCC in the recycled IL to make a spinning dope, that took somewhat longer (40 instead of 15 min) and required higher, 120 °C, temperature, followed by extrusion into a new coagulation bath made by either dissolution of BA-carbamate in the recycled IL or dissolving BA in the recycled IL and forming the carbamate *in situ* through CO_2-bubbling. Fibers were extruded and isolated as noted above. When using the BA-carbamate dissolved in the recycled IL for a coagulation bath, the recovery of the IL was only 84.6%, 55.4% from the coagulation bath and 29.2% from the aqueous washings of fibrous materials. The mass of fibers indicated 91.4% recovery of the biopolymer.

The reusability of recycled IL from *in situ* formed BA-carbamate/IL system was similar. Here, we were able to reclaim 84.3% IL from the coagulation bath and 7.3% IL from aqueous washings of fibrous materials, with a total recovery of 91.6%. Recovery of the biopolymer proceeded with the same efficiency as that during cycle 1, the weight of fibers was 73.1% of the initial cellulose and some fibrous fragments were too tiny to be gathered. Considering that in the first case we observed the same phenomenon, it suggests incomplete conversion of BA into the carbamate.

The volatility of the amine and CO_2 should allow one to use standard techniques to recover and reuse these, however, we note an obvious problem with the recycle of the IL. In the current approach, it is necessary to wash the coagulated biopolymers to recover as much of the IL as possible. While the majority of the IL (~76%–80%) was retained in the coagulation bath, some of the IL (~20%–24%) was found in the aqueous washings of the precipitate or fibers. Separating water from only 25% of the IL is certainly cheaper and less energy intensive than from 100% of the IL, but this will need to be improved further.

4. Conclusions

We have developed a methodology to change the solubility of cellulose and chitin in IL solutions by introducing selected amines and CO_2 to form carbamate salts which results in biopolymer coagulation. In the uncharged state, the amines (TEA, EDA, and BA) are completely miscible with the IL or IL/MCC solution and do not cause coagulation. The addition of CO_2 results in a formation of polar carbamate, that induces phase separation (precipitation) of cellulose. This technology could be used to produce cellulose fibers and films by coagulating MCC/[C_2mim][OAc] solutions into a bath of a 1:1 M mixture of BA-carbamate and [C_2mim][OAc] which was demonstrated on a lab scale. While the carbamate in the coagulation bath could be made *in situ*, there are processing advantages to mixing the preformed carbamate with IL to prepare the coagulating bath.

The [C_2mim][OAc] can easily be recovered because the amine to carbamate transition is reversible, and only a limited amount of water is needed as the wash solvent, but not as coagulant. Among the amines we studied, BA gave the best results because of its low boiling point and low viscosity, which benefited both biopolymer recovery and IL recycle. Using BA, up to 96.4% of the [C_2mim][OAc] could be recovered at the end of first cycle and 84.6% after 2 cycles. Certainly, more research is needed to demonstrate the IL-amine-CO_2 process to be a viable competitor for current biomass processing. Nonetheless, this approach already exhibits some promising features needed to solve the current highly energy-intensive recycling problem of using ILs in biomass processing.

The biggest problems yet to be overcome include recovery of the IL after washing, as this is the only step where some water is introduced into the IL. While the amount of water used for washing the coagulated fibers is significantly less than it would be if water was used for coagulation, decreasing the amount or elimination of all water would improve the economics of the process. Overall, we hope that this work will provide some new directions in research for more economically-viable IL recycling processes in biomass treatment with ILs.

Acknowledgements

The authors thank Dr. Jason Bara for his useful discussion.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gce.2021.07.001.

Supporting Information (SI)

Supporting Information contains: FT-IR spectra of separated solid (MCC, PG-chitin) and the IL ([C_4mim]Cl, [C_2mim][OAc]) from MCC/[C_4mim]Cl/TEA, MCC/[C_2mim][OAc]/EDA, PG-Chitin/[C_2mim][OAc]/EDA, and MCC/[C_2mim][OAc]/BA. Complete characterization for EDA- and BA-carbamate (FTIR, ^{1}H, ^{13}C, COSY, HSQC, HMBC). ^{1}H and ^{13}C NMR analyses for recovered [C_2mim][OAc].

Declaration of competing interests

The authors are named inventors and have financial interest in related patents and patent applications through The University of Alabama and licenses to 525 Solutions, Inc., including US 9394375 which is based on the work reported here. RDR has majority ownership of and is President of 525 Solutions, Inc. and has partial ownership of 525 SDT

LLC, Wyonics LLC, Wyonics-SSG LLC, Consortium for Green Manufacturing LLC, CalAgua Innovations Corp., and Adjacency Labs Corp. JLS is former CSO and former employee of 525 Solutions, Inc., and former CSO of Mari Signum Mid-Atlantic, LLC.

References

[1] J.D. Holbrey, R.D. Rogers, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, first ed., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2002, pp. 41–55.

[2] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, Dissolution of cellulose with ionic liquids, J. Am. Chem. Soc. 124 (2002) 4974.

[3] N. Sun, R.P. Swatloski, M. Maxim, M. Rahman, A.G. Harland, A. Haque, S.K. Spear, D.T. Daly, R.D. Rogers, Magnetite-embedded cellulose fibers prepared from ionic liquid, J. Mater. Chem. 18 (2008) 283–290.

[4] Y. Qin, X. Lu, N. Sun, R.D. Rogers, Dissolution or extraction of crustacean shells using ionic liquids to obtain high molecular weight purified chitin and direct production of chitin films and fibers, Green Chem. 12 (2010) 968–971.

[5] N. Sun, M. Rahman, Y. Qin, M. Maxim, H. Rodríguez, R.D. Rogers, Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate, Green Chem. 11 (2009) 646–655.

[6] C. King, J.L. Shamshina, G. Gurau, P. Berton, N.F.A. Khan, R.D. Rogers, A platform for more sustainable chitin films from an ionic liquid process, Green Chem. 19 (2017) 117–126.

[7] X. Shen, J.L. Shamshina, P. Berton, J. Bandomir, H. Wang, G. Gurau, R.D. Rogers, Comparison of hydrogels prepared with ionic-liquid-isolated *vs.* commercial chitin and cellulose, ACS Sustain. Chem. Eng. 4 (2016) 471–480.

[8] J.-i. Kadokawa, Dissolution, gelation, functionalization, and material preparation of chitin using ionic liquids, Pure Appl. Chem. 88 (2016) 621–629.

[9] J.L. Shamshina, O. Zavgorodnya, J.R. Bonner, G. Gurau, T. Di Nardo, R.D. Rogers, "Practical" electrospinning of biopolymers in ionic liquids, ChemSusChem 1 (2017) 106–111.

[10] O. Zavgorodnya, J.L. Shamshina, J.R. Bonner, R.D. Rogers, Electrospinning biopolymers from ionic liquids requires control of different solution properties than volatile organic solvents, ACS Sustain. Chem. Eng. 5 (2017) 5512–5519.

[11] M. Bagheri, H. Rodríguez, R.P. Swatloski, S.K. Spear, D.T. Daly, R.D. Rogers, Ionic liquid-based preparation of cellulose-dendrimer films as solid supports for enzyme immobilization, Biomacromolecules 9 (2008) 381–387.

[12] J.L. Shamshina, G. Gurau, L.E. Block, L.K. Hansen, C. Dingee, A. Walters, R.D. Rogers, Chitin–calcium alginate composite fibers for wound care dressings spun from ionic liquid solution, J. Mater. Chem. B 2 (2014) 3924–3936.

[13] A. Takegawa, M.-a. Murakami, Y. Kaneko, J.-i. Kadokawa, Preparation of chitin/cellulose composite gels and films with ionic liquids, Carbohydr. Polym. 79 (2010) 85–90.

[14] N. Singh, K.K. Krzysztof, J. Chen, A.J. Patil, J.W. Gilman, P.C. Trulove, W. Kafienah, S.S. Rahatekar, Ionic liquids-based processing of electrically conducting chitin nanocomposite scaffolds for stem cell growth, Green Chem. 15 (2013) 1192–1202.

[15] K. Mundsinger, A. Müller, R. Beyer, F. Hermanutz, M.R. Buchmeiser, Multifilament cellulose/chitin blend yarn spun from ionic liquids, Carbohydr. Polym. 131 (2015) 34–40.

[16] B. Wu, W. Liu, Y. Zhang, H. Wang, Do we understand the recyclability of ionic liquids? Chem. Eur J. 15 (2009) 1804–1810.

[17] P.G. Jessop, D.J. Heldebrant, X. Li, C.A. Eckert, C.L. Liotta, Reversible nonpolar-to-polar solvent, Nature 436 (2005) 1102.

[18] P. Pollet, C.E. Eckert, C.L. Liotta, Switchable solvents, Chem. Sci. 2 (2011) 609–614.

[19] P.G. Jessop, C.A. Eckert, C.L. Liotta, D.J. Heldebrant. Switchable Solvents and Methods of Use Thereof. US Patent US8513464.

[20] J.T. Yeh, H.W. Pennline, K.P. Resnik, Study of CO_2 absorption and desorption in a packed column, Energy Fuels 15 (2001) 274–278.

[21] W.C. Sun, C.B. Yong, M.H. Li, Kinetics of the absorption of carbon dioxide into mixed aqueous solutions of 2-amino-2-methyl-l-propanol and piperazine, Chem. Eng. Sci. 60 (2005) 503–516.

[22] A. Jamal, A. Meisen, C.J. Lim, Kinetics of carbon dioxide absorption and desorption in aqueous alkanolamine solutions using a novel hemispherical contactor-II. Experimental results and parameter estimation, Chem. Eng. Sci. 61 (2006) 6590–6603.

[23] B.P. Mandal, A.K. Biswas, S.S. Bandyopadhyay, Selective absorption of H_2S from gas streams containing H_2S and CO_2 into aqueous solutions of N-methyldiethanolamine and 2-amino-2-methyl-1-propanol, Separ. Purif. Technol. 35 (2004) 191–202.

[24] A.M. Varghese, G.N. Karanikolos, CO_2 capture adsorbents functionalized by amine–bearing polymers: a review, Int. J. Greenh. Gas Control. 96 (2020) 103005.

[25] S.A. Mazari, L. Ghalib, A. Sattar, M.M. Bozdar, A. Qayoom, I. Ahmed, A. Muhammad, R. Abro, A. Abdulkareem, S. Nizamuddin, Review of modelling and simulation strategies for evaluating corrosive behavior of aqueous amine systems for CO_2 capture, Int. J. Greenh. Gas Control. 96 (2020) 103010.

[26] F. T. Gelles, S. Lawson, A.A. Rownaghi, F. Rezaei, Recent advances in development of amine functionalized adsorbents for CO_2 capture adsorption 26 (2020) 5–50.

[27] V.M. Blasucci, R. Hart, P. Pollet, C.L. Liotta, C.A. Eckert, Reversible ionic liquids designed for facile separations, Fluid Phase Equil. 294 (2010) 1–6.

[28] J.E. Bara, D. Camper, D.L. Gin, R.D. Noble, Room-temperature ionic liquids and composite materials: platform technologies for CO_2 capture, Acc. Chem. Res. 43 (2010) 152–159.

[29] D. Camper, J.E. Bara, D.L. Gin, R.D. Noble, Room-temperature ionic liquid-amine solutions: tunable solvents for efficient and reversible capture of CO_2, Ind. Eng. Chem. Res. 47 (2008) 8496–8498.

[30] J. Yang, X. Yu, J. Yan, S.-T. Tu, CO_2 capture using amine solution mixed with ionic liquid, Ind. Eng. Chem. Res. 53 (2014) 2790–2799.

[31] A.I. Akhmetshina, A.N. Petukhov, A.V. Vorontyntsev, A.V. Nyuchev, I.V. Vorotyntsev, Absorption behavior of acid gases in protic ionic liquid/alkanolamine binary mixtures, ACS Sustain. Chem. Eng. 5 (2017) 3429–3437.

[32] M. Ebrahiminejadhasanabadi, W.M. Nelson, P. Naidoo, A.H. Mohammadi, D. Ramjugernath, Investigation of mixed MEA-based solvents featuring ionic liquids and NMP for CO_2 capture: experimental measurement of CO_2 solubility and thermophysical properties, Chem. Eng. Data 66 (2021) 899–914.

[33] D.T. Daly, R.D. Rogers, Y. Qin. Compositions Containing Recyclable Ionic Liquids for Use in Biomass Processing. US Patent US9394375B2.

[34] P.J.G. Huttenhuis, N.J. Agrawal, J.A. Hogendoorn, G.F. Versteeg, Gas solubility of H_2S and CO_2 in aqueous solutions of N-methyldiethanolamine, J. Petrol. Sci. Eng. 55 (2007) 122–134.

[35] A.L. Hohl, R.B. Nielsen, Gas Purification, fifth ed., 1997 (chapter 2): Alkanolamines for Hydrogen Sulfide and Carbon Dioxide Removal, Elsevier, Amsterdam, 2007, pp. 40-186.

[36] J. Li, A. Henni, P. Tontiwachwuthikul, Reaction kinetics of CO_2 in aqueous ethylenediamine, ethyl ethanolamine, and diethyl monoethanolamine solutions in the temperature range of 298−313 K, using the stopped-flow technique, Acc. Chem. Res. 43 (2010) 152–159.