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## Reversible and Non-Reactive Cellulose Separations from Ionic Liquid Mixtures with Compressed Carbon Dioxide

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### Abstract

A novel physical (non-reactive) separation of cellulose from an ionic liquid (IL) / cosolvent mixture by compressed carbon dioxide is presented. The precipitation is completely reversible and rapid within small changes of pressure i.e. liquid phase CO<sub>2</sub> composition. High pressure phase equilibrium, high pressure NMR, and solid state NMR have been utilized to understand the separation phenomena.

Cellulosic biomass is a potential sustainable alternative to petroleum-based feedstocks for fuels and chemicals provided that it is renewable, abundant, and inexpensive with low-energy input and without significantly impacting food sources. However, processing cellulosic biomass is challenging due to its relative recalcitrance to conventional heterogeneous solid-liquid reactions which are mass-transfer limited especially for crystalline biomass types. Only a small number of organic solvents have been discovered that can dissolve even measurable quantities of cellulose.<sup>1</sup> The ability to dissolve biomass can significantly aid in separations of the constituent components (e.g. cellulose, lignin, etc.) and can significantly decrease the reaction time or reactor size required to transform biomass to various chemicals and fuels. Some ionic liquids (ILs) have the highest known solubilities of cellulose at any given temperature.<sup>1a</sup> Furthermore, select ILs including 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIm][DEP], see Figure 1) have demonstrated success for cellulose dissolution and pretreatment using antisolvent precipitation.<sup>1a, 2</sup> The precipitated cellulose product is highly amorphous which has been correlated to superior chemical and biochemical conversion rates to glucose or other chemicals even despite the heterogeneous reaction scenario.<sup>3</sup>

While significant interest has been given to cellulose dissolution, only limited work has investigated the ensuing biomass precipitation step and necessity for IL recycling. The majority of aqueous and organic solvents have no intrinsic cellulose solubility and most act as “antisolvents” when added to IL/cellulose mixtures leading to cellulose precipitation. Typical antisolvents in the literature are chosen among polar protic liquids (H<sub>2</sub>O, EtOH, etc.) and are added in mass ratios of 1:1 (Antisolvent:IL-Cellulose), 2:1 and greater. These

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antisolvents induce cellulose precipitation by disrupting cellulose-IL hydrogen bonding producing mostly amorphous cellulose.<sup>4</sup> Protic antisolvents are so highly effective at precipitating biomass from ionic liquids that recent solubility studies in our group indicate that even trace amounts of these residual compounds in the ionic liquid can significantly inhibit further biomass dissolution. For example, we have found that cellulose solubility in [EMIm][DEP] at 40 °C is reduced by more than 55% with only 1 % mass of residual water in the IL.<sup>5</sup> Thus, the IL must be highly purified prior to recycle for further processing.

To assess the energy requirements of IL purification we performed a series of simulations based on thermodynamic models fit to experimental vapor-liquid equilibrium (*VLE*) data of IL/antisolvent systems.<sup>6</sup> Using the Peng-Robinson equation of state (PR EoS), we estimate the separation of a 1:1 mass ratio of [EMIm][DEP] to water using vacuum flash distillation at 0.01 bar and 175°C would consume over 20 MJ of heat per kg cellulose processed (not including mechanical (vacuum) power), based on an assumed practical cellulose solubility limit of 15 %mass. For comparison, the energy content (heat of combustion) of cellulose is between 16-18 MJ/kg.<sup>7</sup> Thus, more energy would be consumed by the IL/water separation process than the energy content of the pretreated cellulose. Other antisolvents and lower quantities could reduce separation energies, but the energy demand is still predicted to be of the same order of magnitude. Therefore, quantitative separation of the IL and liquid antisolvent for recycle is predicted to be highly energy intensive and could impede large-scale viability.

Barber *et al.* have recently demonstrated the use of carbon dioxide as a reactant to precipitate cellulose from imidazolium ionic liquids with specifically acetate anions [Ac], e.g. [EMIm][Ac].<sup>8</sup> The IL-CO<sub>2</sub> reaction produces a mixture of 1-alkyl-3-methylimidazolium-2-carboxylate zwitterion and acetic acid which is unable to solubilize cellulose.<sup>9</sup> However, this process requires workup, regeneration, and separation procedures to restore the ionic liquid for reuse which further adds to the energy requirements and process complexity.

A non-reactive, low-energy process for the precipitation of cellulose from ionic liquids would be highly useful for biomass pretreatment. Here we demonstrate for the first time the use of compressed carbon dioxide as a physical (non-reactive) antisolvent for the precipitation of cellulose from IL/cosolvent mixtures. A model system is presented using [EMIm][DEP] and a variety of cosolvents, focused primarily on dimethylformamide (DMF) for illustration purposes. This interesting phase behavior demonstrates the feasibility of using CO<sub>2</sub> composition as a separation switch for the precipitation of cellulose from ionic liquid mixtures.

We and other groups have found that some polar aprotic molecules do not significantly decrease cellulose solubility in mixtures of ionic liquids up to certain compositions.<sup>10</sup> The presence of these “cosolvents” significantly improves the transport properties (viscosity, diffusivity, etc.) of IL/cellulose solutions which are commonly cited as a limitation of biomass processing with ILs. Select cosolvents also offer advantages in this CO<sub>2</sub>-based separation process since many polar aprotic molecules exhibit relatively high CO<sub>2</sub> solubilities.<sup>11</sup> In addition, the presence of CO<sub>2</sub> itself decreases the mixture viscosity, further enhancing transport properties.<sup>12</sup> In initial studies without cosolvents, only small quantities

of precipitated cellulose were observed using compressed CO<sub>2</sub> even to high pressures. Thus, the cosolvent plays an ancillary but necessary role in intensifying the separation phenomena. In this study, microcrystalline cellulose (Figure 2a) was dissolved in a model system of ionic liquid [EMIm][DEP] with select DMF cosolvent ratios. Compressed carbon dioxide was added to the IL/DMF/cellulose liquid mixture resulting in vapor-liquid equilibrium with an IL/cosolvent/cellulose liquid phase and a CO<sub>2</sub>-rich vapor phase absent of cellulose and the IL (Figure 2b). At certain pressures (CO<sub>2</sub> compositions), cellulose dramatically precipitated from the liquid mixture forming a solid-liquid-vapor equilibrium (*SLV*) condition (Figure 2c): solid cellulose, IL/cosolvent-rich liquid, CO<sub>2</sub>-rich vapor. During the precipitation either a single mass of amorphous cellulose or a range of cellulose particles could be produced depending on the rate of CO<sub>2</sub> addition, mixing speed, etc.

With a small pressure reduction to just a few bar below the precipitation point, cellulose re-dissolved in the liquid phase, and a clear homogeneous mixture (Figure 2b) was recovered within minutes. Therefore, a narrow pressure/ composition regime exists in which cellulose undergoes a transition to virtually no solubility in the IL/cosolvent liquid phase.

In order to recover a solid cellulose sample in our current experimental setup, a portion of cellulose was isolated above the IL/cosolvent liquid level and collected immediately upon depressurization before re-dissolution could occur by contact with the IL-phase. Subsequently, the sample was washed with ethanol to remove any residual IL (Figure 2d), dried and analyzed. The amount of residual IL is a function of the precipitation parameters such as stirring and particle size. Based on these initial experiments we believe the washing step could be eliminated or reduced through further experimental design of a separation vessel capable of physically preventing contact between precipitated cellulose and the IL mixture at process pressure.

Table 1 illustrates cellulose separation conditions (*SLV*) at 25 °C and 40 °C for two ionic liquids, five cosolvents, and two cosolvent compositions. For the system of 5 %mass cellulose dissolved in a mixture of 75 %mass [EMIm][DEP] and 25 %mass cosolvent DMF at 25 °C, (IL/cosolvent compositions given on a solute-free basis) the precipitation occurs at just 32 bar of pressure. Thus, the separation occurs by simply introducing CO<sub>2</sub> in its vapor phase at conditions much lower than its vapor pressure or critical point (31.1 °C, 73.8 bar). For the same system at 40 °C the precipitation pressure increases to 49 bar which is likely due to the decreased solubility of CO<sub>2</sub> in the liquid phase at elevated temperatures. Increasing the proportion of DMF in the mixture to an initial 50 %mass (solute-free basis) loading at 25 °C results in a lower separation pressure of 26 bar. However at 40 °C, the 50 %mass and 25 %mass DMF mixtures with 5 %mass cellulose both precipitate at approximately 49 bar. These results indicate that increased cosolvent loading can lower the required separation pressure at select conditions.

For the 50 %mass DMF/IL system, the effect of cellulose composition on the separation point was measured. With a 2% cellulose loading, the precipitation pressure increases to 33 bar, while at 8% cellulose the pressure decreases to 24 bar compared to the 5% cellulose pressure of 26 bar.

Although pressure has been discussed as an operating parameter for the separation, it is the concomitant increase in CO<sub>2</sub> composition with pressure not hydrostatics that is the main driving force for cellulose precipitation.

Other cosolvents were investigated with a 5 % mass cellulose loading. For the 25 % mass DMSO cosolvent system at 25 °C, the precipitation occurs at 54 bar which is 22 bar higher than DMF at the same cosolvent to IL mass ratio. However, the molar ratios of these cosolvent/IL systems are 55 % mole DMSO vs. 78 % mole DMF, potentially explaining the difference in the observed precipitation points. Interestingly, cellulose did not precipitate from [EMIm][DEP] at 40 °C with 25 % mass DMSO up to 250 bar pressure. Therefore, it is evident that cosolvent selection and loading have a significant impact on the separation conditions. In addition, the ionic liquid 1-butyl-3-methylimidazolium chloride [BMIm][Cl] was investigated since it also demonstrates large cellulose solubilities in the literature. However, no precipitation was observed with this ionic liquid and these particular cosolvents at an initial loading of 25 % mass cosolvent and 5 % mass cellulose.

To confirm the physical (non-reactive) interactions between [EMIm][DEP] and CO<sub>2</sub>, high pressure coupled <sup>1</sup>H-<sup>13</sup>C NMR was measured. [EMIm][DEP] was exposed to CO<sub>2</sub> at 100 bar pressure for 72 hours to ensure equilibrium had been established. For reactive ILs with CO<sub>2</sub> such as [EMIm][Ac], the carboxylation of the imidazole ring produces a NMR resonance at ≈ 155 ppm.<sup>9</sup> As shown in Figure 3, the NMR spectra of [EMIm][DEP] at 100 bar does not indicate a strong peak for the carboxylate at 155 ppm even after 72 hours of exposure. Based on the signal-to-noise ratio, any carboxylate would be less than 1 % mole. Thus, the separation presented herein occurs by a physical, non-reactive, process. The reaction mechanism between CO<sub>2</sub> and 1,3-dialkyl-imidazolium acetate ILs is believed to occur in two steps: 1) deprotonation of the bridging carbon (C2) in the imidazolium ring by the basic acetate anion to an imidazole carbene; 2) CO<sub>2</sub> reaction to form a stable carboxylate product.<sup>9</sup> The diethyl phosphate anion is less basic (pKa ~1.4; at least in aqueous solution and presumed in ILs), compared to the acetate anion (pKa 4.75), and is unable to be active in the deprotonation of the imidazolium cation. Additional <sup>1</sup>H and <sup>13</sup>C NMR experiments have been conducted on pre- and post- pressurized [EMIm][DEP] and the results further confirm the IL stability (see supplemental data file).

Solid phase analysis of the cellulose product was performed by CP/MAS solid state NMR. Figure 4 displays the spectra of microcrystalline (pre-processed) and post-processed amorphous cellulose. Crystalline cellulose is characterized by sharp C<sub>4</sub> and C<sub>6</sub> peaks at 92 and 68 ppm respectively which are most actively involved in inter- and intra- molecular hydrogen bonding.<sup>1b, 13</sup> As shown, the C<sub>4</sub> and C<sub>6</sub> peaks of precipitated cellulose shift and broaden indicating reduced crystallinity. Degree of cellulose crystallinity was quantified using the C<sub>4</sub> peak separation and integration method.<sup>13b, 14</sup> Native microcrystalline cellulose exhibited 61% crystallinity while the processed amorphous cellulose displayed <11% crystallinity. Therefore, total cellulose crystallinity was reduced by 80+% through IL/ cosolvent and CO<sub>2</sub> antisolvent processing.

Simulation studies show that ionic liquid solvation of cellulose is largely attributed to the disruption of inter and intra molecular hydrogen bonds within the crystalline cellulose

structure by the IL anion.<sup>15</sup> Additional spectroscopic and simulation studies show that dissolved CO<sub>2</sub> preferentially interacts with ionic liquid anions.<sup>16</sup> The presence of aprotic cosolvents, in limited amounts, does not seem to disrupt anion stabilization of dissolved cellulose to any great extent. Thus, the presence of CO<sub>2</sub> must interfere with the ability of the IL anion to solvate cellulose.

The required energy of this novel process stems from the compression of CO<sub>2</sub>; for example from 1 bar to 26-54 bar at 25°. Our EoS prediction indicates that this compression process would only require 1.1-1.4 MJ of mechanical energy per kg of cellulose processed; thus requiring an order of magnitude less energy than the thermal distillation process with liquid antisolvents, *i.e.* ~20MJ/kg heat. While mechanical energy is more costly than heat, there is still significant potential energy savings for this new process.

Current experiments are attempting to ascertain the phase equilibrium of CO<sub>2</sub>/cosolvent/IL systems to determine the quantitative composition of CO<sub>2</sub> at the separation conditions presented.<sup>6</sup> For instance, CO<sub>2</sub> solubility in the 25 % mass DMF/IL mixture at the measured precipitation pressure at both 32 bar at 25°C and 49 bar at 40°C is similarly ~39 % mole. Additionally, at a DMF loading of 50 % mass the cellulose precipitation pressures are 26 bar and 49 bar for the same two temperatures corresponding to CO<sub>2</sub> compositions in the mixed solvent of 31 and 42 % mole respectively. From these preliminary results it is evident that cellulose precipitation occurs in a relatively narrow range of CO<sub>2</sub> compositions. In addition, the volume of the IL/cosolvent mixture increases by up to 30% with increasing composition of CO<sub>2</sub>. This leads to a nominal decrease in ionic liquid concentration (moles per volume) or, more importantly for cellulose solubility, a lower concentration of the IL anion.

In summary, this communication demonstrates the first physical (non-reactive) and reversible precipitation of cellulosic biomass from an ionic liquid mixture using compressed carbon dioxide. High pressure NMR confirms that precipitation does not occur via chemical reaction with CO<sub>2</sub>. Solid state NMR indicates an 80+% reduction in cellulose crystallinity. Cellulose precipitation is driven by liquid phase composition of carbon dioxide which dramatically reduces the cellulose solubility after a critical composition is obtained.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

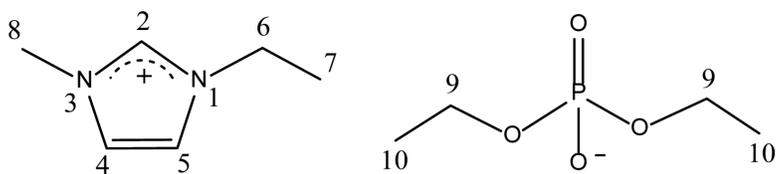
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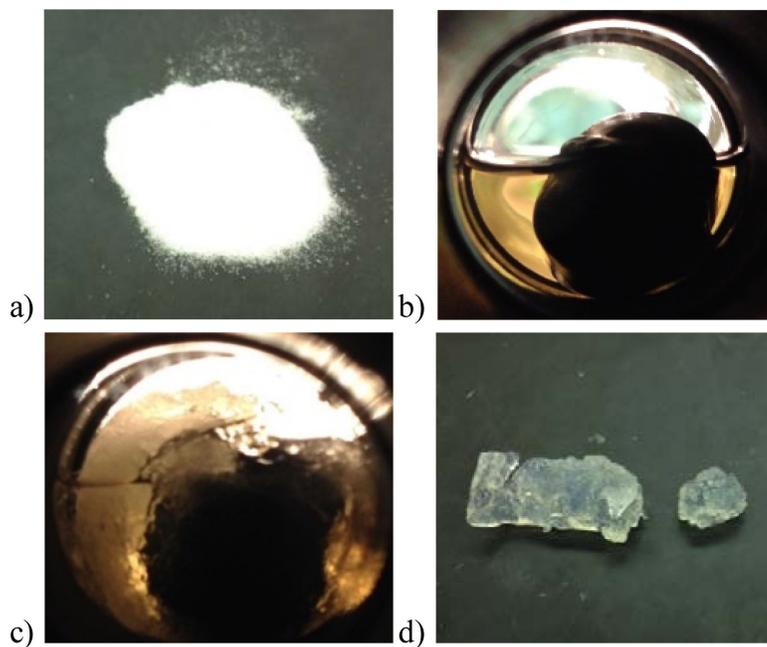
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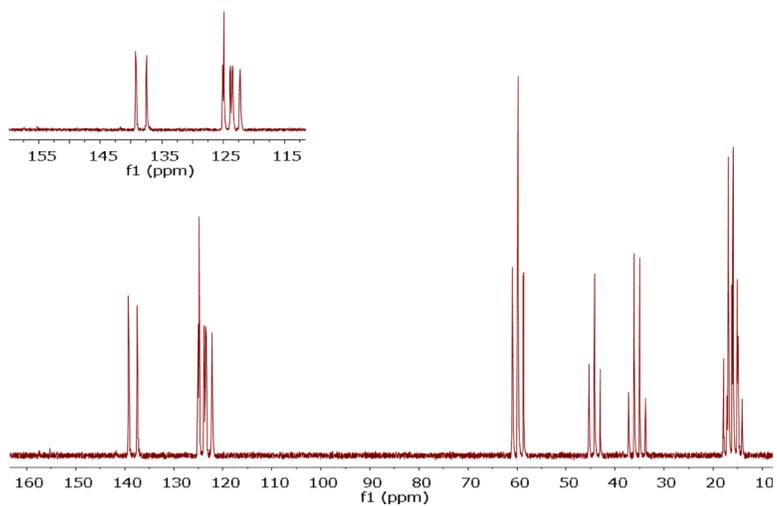
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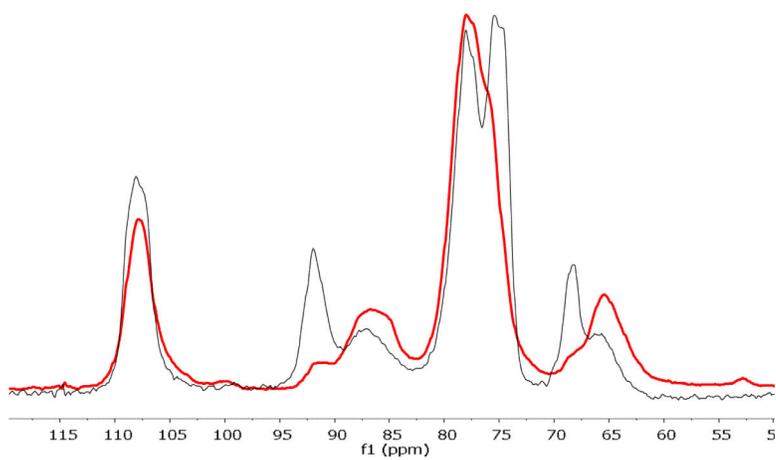
**Figure 1.**  
1-Ethyl-3-Methylimidazolium Diethyl Phosphate [EMIm][DEP] Structure.



**Figure 2.** Images of a) micro-crystalline cellulose; b) cellulose /IL/DMF (stirbar in windowed-pressure vessel); c) cellulose precipitating with CO<sub>2</sub>; d) precipitated cellulose (washed).



**Figure 3.** [EMIm][DEP]-CO<sub>2</sub> high-pressure coupled  $^1\text{H}$ - $^{13}\text{C}$  NMR at 100 bar after 72 hours. Inset: absence of resonance in imidazolium carboxylate region.



**Figure 4.** CP/MAS  $^{13}\text{C}$  NMR on native microcrystalline cellulose (black) and processed amorphous cellulose (red).

**Table 1**

Incipient conditions of cellulose precipitation (SLV Equilibrium) from IL/cosolvent mixtures with compressed CO<sub>2</sub>

Ionic Liquid	Cellulose Loading [%mass]	Co-solvent	Cosolvent Loading <sup>a</sup> [%mass] (%mole)	Precipitation Pressure CO <sub>2</sub> [bar]	
				25°C	40°C
[EMIm][DEP]	5%	Acetone	25% (60.2%)	34	--
	5%	ACN	25% (68.2%)	43	62
	5%	DMF	25% (54.8%)	32	49
	2%	DMF	50% (78.3%)	33	na
	5%	DMF	50% (78.3%)	26	49
	8%	DMF	50% (78.3%)	24	na
	5%	DMSO	25% (54.8%)	54	--
	5%	DMI	25% (43.5%)	53	68
[BMIm][Cl]	5%	DMSO	25% (42.9%)	--	--
	5%	DMF	25% (44.5%)	--	--

"--" indicates that precipitation did not occur at CO<sub>2</sub> pressures up to 250 bar; *na* not attempted

<sup>a</sup> solute-free composition