Ionic Liquids

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# Coagulation of Chitin and Cellulose from 1-Ethyl-3-methylimidazolium Acetate Ionic-Liquid Solutions Using Carbon Dioxide**

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Interest in using ionic liquids[1] (ILs) within a lignocellulosic biorefinery is due in part to their ability to dissolve biopolymers such as cellulose,[2,3] hemicellulose,[4] and lignin,[4] as well as raw biomass.[4–9] We and others have proposed extending the biorefinery concept to ocean-based biopolymers using ILs for the dissolution, extraction, and electrospinning of chitin from crustacean shells.[10–13] However, one key processing step needing improvement is recycling of the IL after an antisolvent (e.g., water or ethanol) is added to coagulate the dissolved biopolymers by solvating the IL.[7,14] Distillation can be used to remove the antisolvents from the IL, however, the energy intensive process presents economic and engineering challenges at large scale.[14,15] We have been searching for alternatives to high-boiling liquid antisolvents that would promote facile separation from the IL.

We recently reported the chemisorption of $CO_2$ in 1-ethyl-3-methylimidazolium acetate ([$C_2$mim][OAc]) through chemical reaction of an in situ carbene with $CO_2$ and isolated crystalline [$C_2$mim][$H(OAc)_2$][$C_2mim^+$-$COO^-$].[16] Formation of the zwitterion produces one mole of acetic acid, which forms hydrogen bonds with the strongest acceptor, any remaining acetate anion. Since supercritical carbon dioxide ($scCO_2$) is inexpensive, nonexplosive, highly available, easy to remove from extracted products, and is considered to be the most suitable fluid in supercritical processes,[17–20] we explored whether $scCO_2$ (or even $CO_{2(g)}$) could be used as a coagulation solvent for biopolymer–IL solutions. We hypothesized that if $CO_2$ reacted with [$C_2$mim][OAc], even when a biopolymer was dissolved in it, the biopolymer would precipitate and the IL could be recycled easily through the stoichiometric addition of water (Scheme 1). To test our hypothesis, we chose to focus first on the coagulation of chitin extracted from dried shrimp shells with [$C_2$mim][OAc], because of its higher molecular weight than commercially available practical grade or pure chitin which we anticipated would be more easily coagulated because of its lower solubility.[11,13] This would give access to a superior and valuable biopolymer, which cannot be obtained using the current harsh and energy-intensive extraction processes, and thus might allow the use of a slightly more expensive process.

A solution of chitin extracted from dried shrimp shell (0.6 g) with [$C_2$mim][OAc] (29.4 g) was prepared using a microwave process described previously.[11,13] Aliquots of the extract solution (5–6 g) were then loaded into a high-pressure windowless reactor (see Figure S1 in the Supporting Information) at room temperature, the reactor was purged and filled with $CO_{2(l)}$ to 6.2 MPa, and then sealed. The batch reactor was heated to 35–40 °C increasing the pressure to 7.6–10.3 MPa, above the critical pressure. Separate samples were contacted with $scCO_2$ for 1, 2, or 4 h. After depressurization, a phase boundary was observed across the fluid interface (Figure 1 b). The film initially inhibited the release of $CO_2$ from the IL-rich phase until overcome by the gas pressure (Figure 1 c). The solid film was then physically removed from the IL surface using forceps.

Infrared spectroscopy of the solid film confirmed chitin with residual IL. The adhering IL was easily removed from the chitin by minimal addition of water during which $CO_2$ effervescence was observed (Figure 1 d). (The addition of water as a purification step was employed only to remove the IL for measurement of recovery yields and could be exchanged for thermal or physical separation in the process design.) The chitin (Figure 1 e) was dried to constant weight and the absence of IL was confirmed by IR spectroscopy (Figure S2). The yields based on the mass recovered and the available chitin in the shrimp shells (22 ± 1 %) were 19 ± 4 % (1 h contact), 21 ± 6 % (2 h), and 20 ± 7 % (4 h). We previously reported that using water as the coagulation solvent, up to 94 % of the available chitin could be recovered.[11] The low yield here and the observation of gas trapped in the IL-rich

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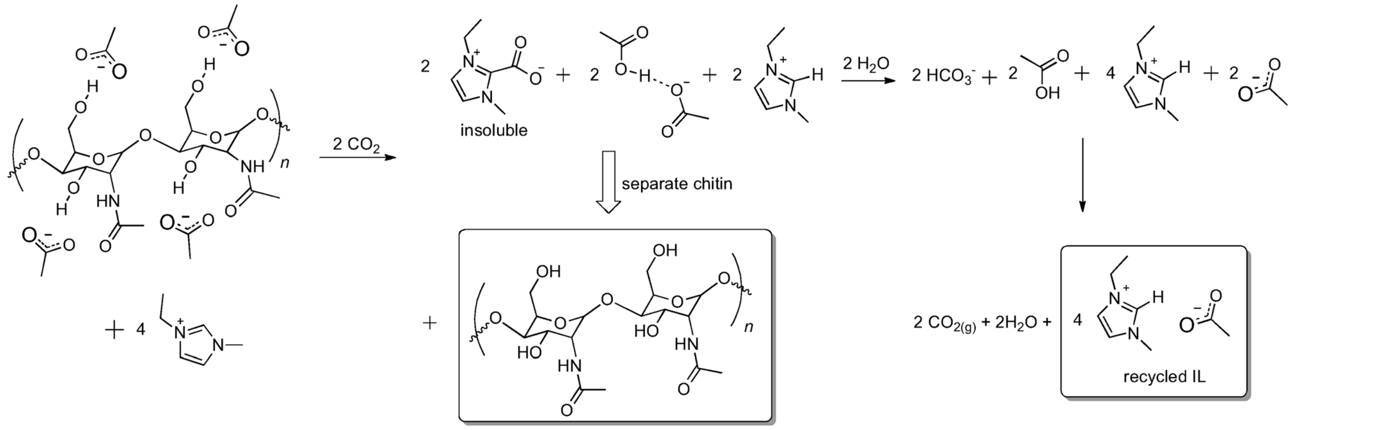


***Scheme 1.*** Formation of a carboxylate zwitterion[16] from the chemisorption of $CO_2$ with [$C_2$mim][OAc] produces acetic acid which competes for solubilizing acetate anions resulting in precipitation of chitin from the solution. Addition of water produces bicarbonate which reacts with acetic acid to regenerate [$C_2$mim][OAc].

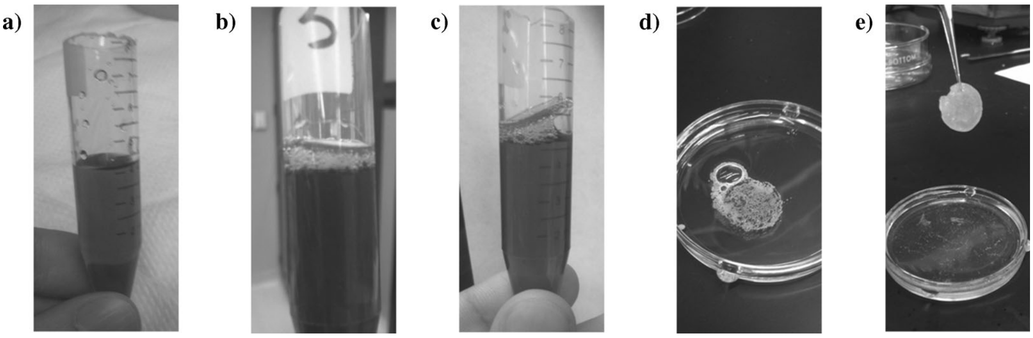


***Figure 1.*** The coagulation of chitin from a solution of shrimp shell extract in [$C_2$mim][OAc]. a) The extract solution, b) the coagulated chitin film, c) the coagulated chitin film being lifted by the pressure of the gas, d) the film once placed in water, and e) the chitin film removed from water.

phase of the solution beneath the film led us to hypothesize that further coagulation was prevented by limited mass transfer and reaction only at the fluid interface.

We then attempted to determine if increased chitin recovery could be obtained with a sequential batch system at 1 h contact times followed by film removal after each contact. Two different chitin solutions were compared, one from direct extraction of 2 wt% dried shrimp shell and a second by dissolution of 1.75 wt% of regenerated chitin (previously extracted and coagulated). Approximately 5–6 g samples of each solution were loaded into the reactor and pressurized with $CO_2$ for 1 h as described above. The samples were then weighed to measure the amount of $CO_2$ absorbed, followed by removal of the surface film. This entire process was repeated until the entire solution was solidified, which depending on the solution was 5–7 times. Each film was washed with a minimal volume of water to remove the residual IL (ca. 7% of the original IL volume per film) and dried to constant weight for yield determination. Infrared spectroscopy indicated each sequential film was of equal purity and quality (Figure S3).

Figure 2 summarizes the cumulative chitin recovery and the mass of chitin coagulated for each sequential 1 h contact time (Table S1). The mass of chitin recovered after each 1 h contact was $5.1 \pm 0.9$ mg and $10 \pm 2$ mg for the shrimp shell extract and regenerated chitin solutions, respectively, indicating that coagulation in this batch reactor was indeed limited to the fluid interface. Nonetheless, 95% of the available chitin in the shrimp shells was recovered from the extract solution (about 0.45% chitin in solution) and 57% of the chitin in the much more concentrated regenerated chitin solution (1.75%) after $5 \times 1$ h contacts. We believe the higher recoveries from the extract solution are due to the presence of other dissolved material from the shrimp shells (e.g., $CaCO_3$)

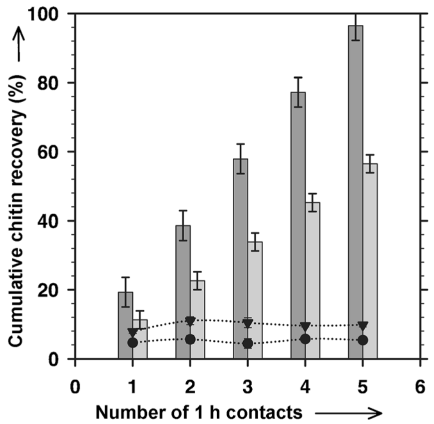


***Figure 2.*** Cumulative chitin recoveries (left axis, bars) and mass of chitin recovered per 1 h contact (right axis, •••••) from solutions of chitin extracted from shrimp shells (dark gray and ●) and regenerated chitin (light gray and ▼). Error bars are from triplicate measurements.

  

which would reduce the number of free acetate anions available to dissolve the chitin.

After three 1 h contacts, a crystalline solid was observed at the bottom of both sample vials, which quickly liquefied when exposed to air. Using a nitrogen atmosphere to prevent hydrolysis, $^1$H NMR in DMSO of the solid (Figure S4) confirmed formation of the carboxylate zwitterion [$C_2$mim$^+$-$COO^-$]. This suggests that the mechanism for the chitin coagulation is as in Scheme 1, where the formation of the zwitterion liberates acetic acid which in turn ties up acetate anions, effectively removing two anions from those available to solvate the chitin.

Since we have previously shown that the reaction of [$C_2$mim][OAc] with $CO_2$ also occurs at room temperature and pressure, we hypothesized that it should also be possible to coagulate chitin by sparging gaseous $CO_2$ through the solution at room temperature. We prepared 5 g of a 1.75 wt% solution of regenerated chitin in [$C_2$mim][OAc] as above in a 20 mL scintillation vial and bubbled $CO_2$ through the solution at atmospheric pressure using a syringe. After about 3 h, the solution became so viscous that no further bubbling could be observed. Although we could not observe a chitin precipitate, we were able to confirm carboxylate formation via $^1$H NMR spectroscopy (see the Supporting Information). This suggests that while gaseous $CO_2$ agitates the system creating a viscous mixture, sc$CO_2$ decreases the viscosity allowing for the separation of the components.

For comparison, we repeated the experiment with a 5 wt% solution of microcrystalline cellulose (MCC, DP = 270) in [$C_2$mim][OAc] (6.5 g), prepared by microwave dissolution. After bubbling $CO_{2(g)}$ through the clear solution for 3 h, a precipitate was observed (Figure S5) which was confirmed by IR spectroscopy to be pure MCC. After continued bubbling for a total of 10 h, the solution solidified into a thick, gritty paste. Powder X-ray diffraction analysis of the paste confirmed the presence of both MCC and [$C_2$mim][H(OAc)$_2$][$C_2$mim$^+$-$COO^-$] (Figure S6). Upon standing for several minutes, the paste absorbed water from the air and effervesced, resulting in a flocculent solid (MCC) suspended in IL. Using this experimental setup it was not possible to separate cellulose and therefore quantification of the MCC recovery was not possible.

To confirm the role of the acetate anion in the coagulation mechanism, we repeated the MCC experiment above, but used an IL with a less basic anion 1-butyl-3-methylimidazolium chloride ([$C_4$mim][Cl]). After sparging $CO_{2(g)}$ through a 5 wt% solution of MCC in [$C_4$mim][Cl] in the same manner as above, no precipitate nor viscosity changes were observed. In addition, no reaction was observed when this solution was contacted with sc$CO_2$ (Figure S7). These results suggest that with the less basic chloride anion, the IL is not reactive enough with $CO_2$ for biopolymer coagulation.

While contact with either gaseous or sc$CO_2$ does provide a method for the coagulation of chitin or cellulose from [$C_2$mim][OAc] solution, a potential purification problem remains in finding a low-energy method to remove and recycle any residual IL from the biopolymer. We made several attempts to remove the IL completely from the chitin films using only $CO_2$ (without using water or other antisolvents). Coagulated chitin films with residual IL were placed in a porous metal basket and contacted with sc$CO_2$ within the static high-pressure reactor for several hours. Although the residual IL had adsorbed some $CO_2$, IL remained on the film. The same result was obtained when the samples were continually purged in the reactor with liquid $CO_2$ at 6.2 MPa for 1 h.

We also considered more conventional techniques such as pressing or heating. Some of the residual IL could be removed by simply suspending and heating the films to decrease the viscosity of the IL and allowing it to drip off. In one experiment, after the suspended film was heated for 12 h at 100 °C, up to 82% of the IL was removed; however, at these temperatures, there is no recycling advantage over using water or ethanol as the antisolvent.

For IL recycling to provide a cost-advantage, minimal energy must be used in the recovery process of the IL from the coagulation solvent. Though we have greatly decreased the amount of water used in the coagulation process by being able to concentrate the chitin from the chitin/IL solution using $CO_2$, a purification step is required through use of water or heat to remove the residual IL. We can envision an optimized process that would coagulate the biopolymer using sc$CO_2$ in a continuous flow reactor where the biopolymer material would then be stripped of the majority of the residual IL through physical separation. The final purification step may still require water, however, this amount might be stoichiometric and used for IL regeneration from the carboxylate zwitterion as shown in Scheme 1.

Overall, we have demonstrated that the chemisorption of $CO_2$ is a viable mechanism for coagulation of chitin and cellulose dissolved in [$C_2$mim][OAc] using sc$CO_2$ and $CO_{2(g)}$ through the zwitterionic imidazolium carboxylate that sequesters the acetate anions from the system thus precipitating the biopolymer. The advantage of using sc$CO_2$ over $CO_{2(g)}$ is a cleaner, density-based physical separation, where the less dense chitin remains at the liquid interface, while the more dense crystalline [$C_2$mim][H(OAc)$_2$][$C_2$mim$^+$-$COO^-$] settles to the bottom. This density-based separation might be amenable to continuous processing, however, because ILs are not generally soluble in $CO_2$,[21] removal of all residual IL from the precipitated biopolymer remains a significant challenge.

The use of $CO_2$ chemisorption as an alternative coagulating process has the potential to provide an economical and energy-efficient method for recycling the IL by eliminating the need to distill higher boiling coagulation solvents from the IL, or at least reducing the amount of antisolvent which must be removed. For example, in our non-optimized proof of concept, only approximately 34% of the IL (residual IL which was washed from the chitin films after sc$CO_2$ coagulation) would require removal of liquid antisolvent (here water) to be recycled. Even this, however, can be greatly improved upon using other low-energy techniques we are currently exploring. Clearly the continuing challenge will be balancing the energetic costs of IL recycle with the economic value of the biopolymer. While perhaps not the final answer, and with many engineering parameters to be determined, this coagulation route should be considered when [$C_2$mim][OAc] or closely related ILs are chosen as the biopolymer dissolution solvent.

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