Electronic Supplementary Information (ESI)

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

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SI 1. Experimental Procedures

1.1. Materials

Ionic liquid 1-ethyl-3-methylimidazolium diethyl phosphate [EMIm][DEP] was synthesized from 1-methylimidazole (Acros Organics 99%) and triethyl phosphate (Sigma Aldrich 99.9%) using a microwave reactor (Biotage Initiator). Synthesis was conducted at 170 ^{o}C for one hour. Subsequently the IL was washed three times with ethyl acetate (Fisher 99.9%) and vacuum dried for a minimum of 24 hours. IL purity was measured by NMR to be >99.9%. Ionic liquid 1-butyl-3-methylimidazolium chloride [BMIm][Cl] was synthesized from 1-methylimidazole (Acros Organics 99%) and 1-chlorobutane (Sigma Aldrich >99.8%). Synthesis was conducted according to previously described methods and purity was measured by NMR to be >99.9%. Organic solvents acetone (Sigma Aldrich >99.9%), acetonitrile (Sigma Aldrich >99.9%), dimethylformamide (Fisher Scientific >99.8%), dimethyl sulfoxide (Sigma Aldrich >99.9%), and dimethyl imidazolidinone (TCI Chemical >99%) were stored under inert atmospheres of argon and dried by molecular sieves (Fisher Scientific 4Å). Microcrystalline cellulose powder (Sigma Aldrich) was used as received. Carbon dioxide (Matheson 99.99%) was used as received. Water content of all liquid chemicals was measured prior to use by Karl Fisher coulometric titration (Mettler Toledo DL32). Water contents are listed as follows: 1-ethyl-3-methylimidazolium diethyl phosphate (179 ppm), 1-butyl-3-methylimidazolium chloride (430 ppm), acetone (322 ppm), dimethylformamide (126 ppm), dimethyl sulfoxide (63 ppm), dimethyl imidazolidinone (400 ppm).

1.2. Precipitation Studies

Mixtures of IL [EMIm][DEP] and co-solvent (DMF used here for illustration purposes) were prepared in sealed glass vials and mechanically mixed by a rare earth metal magnetic stir bar. Microcrystalline cellulose was fed into the vial at 80 ^{o}C with constant mixing. Cellulose was dissolved in approximately 10 minutes. The homogeneous IL/DMF/cellulose solution was then cooled to room temperature and loaded into a steel autoclave cell. The resulting cellulose compositions at room temperature were always sub-saturated. Compressed CO_2 was added into the autoclave cell by a high-pressure syringe pump (ISCO 260D) and temperature was maintained by a thermostatic hot plate (IKA RCT Basic). CO_2 was dosed to a loading just prior to cellulose precipitation and allowed to equilibrate for approximately 20 minutes. Mixing inside of the autoclave was accomplished by a stir bar. After reaching equilibrium an additional small quantity of CO_2 was added to the cell and cellulose precipitation was visually determined by cloud point analysis, rapid viscosity increase, and the presence of solid amorphous cellulose within the cell. Precipitation trials were repeated in triplicate both from lower to higher pressure and higher pressure to lower pressure to confirm the separation point.

1.3. Solution State NMR

Liquid phase ambient pressure NMR experiments were performed on a Bruker Avance 500 MHz NMR-spectrometer under ambient conditions. Samples were prepared in 5mm NMR tubes with co-axial inserts to prevent contact of the deuterated lock solvent (DMSO-d6 99.9% Cambridge Isotopes) and sample. ^{1}H NMR acquisition parameters consisted of 16 scans with a delay time (d1) of 1 second. Spectral analysis was performed using MestReNova 9 software. Characteristic peaks of [EMIm][DEP] include δ 9.87 (s, 1H), 7.97 (s, 1H), 7.87 (s, 1H), 4.23 (q, 2H), 3.89 (s, 3H), 3.64 (m, 4H), 1.40 (t, 3H), and 1.05 (t, 6H).

1.4. High Pressure NMR

High pressure NMR experiments were performed in sealed 10mm sapphire NMR tubes. Gravimetrically prepared samples were loaded into the NMR tube and pressurized to 100 bar by a syringe pump (ISCO 260D). Samples were provided 72 hours to equilibrate prior to testing. A Bruker Avance 500 MHz NMR-spectrometer was used to process the samples. Due to a broken proton channel, only coupled ^{13}C-^{1}H results were obtained. This data was still able to provide conclusive evidence that no reaction between CO_2 and [EMIm][DEP] occurred. Acquisition parameters for the high pressure NMR consisted of 128 scans with a delay time (d1) of 5 seconds. Characterization of the coupled ^{1}H-^{13}C spectra is as follows: C_2 (137ppm), C_4 (124 ppm), C_5 (122 ppm), C_6 (36 ppm), C_7 (44 ppm), C_8 (15 ppm), C_9 (60 ppm), C_{10} (16 ppm). [EMIm][DEP] structure and carbon numbering provided in Figure 1.

1.5. Solid State NMR

Cross polarization/magic angle spinning (CP/MAS) solid state ^{13}C NMR experiments were performed on a Bruker Avance 500 MHz spectrometer. Spectral parameters were set at 10240 scans with a relaxation delay time of 1 second. Newman's C_4 peak separation method was applied to calculate cellulose crystallinity. Crystalline cellulose is represented by the C_4 peak at 92 ppm while the amorphous cellulose C_4 peak is located at 87ppm. Degree of crystallinity was calculated by taking the ratio of integrated C_4 crystalline peak height to total C_4 peak height.

Additional information is provided in detail by Park et al.[13b, 14]

SI 2. Supplemental Figures

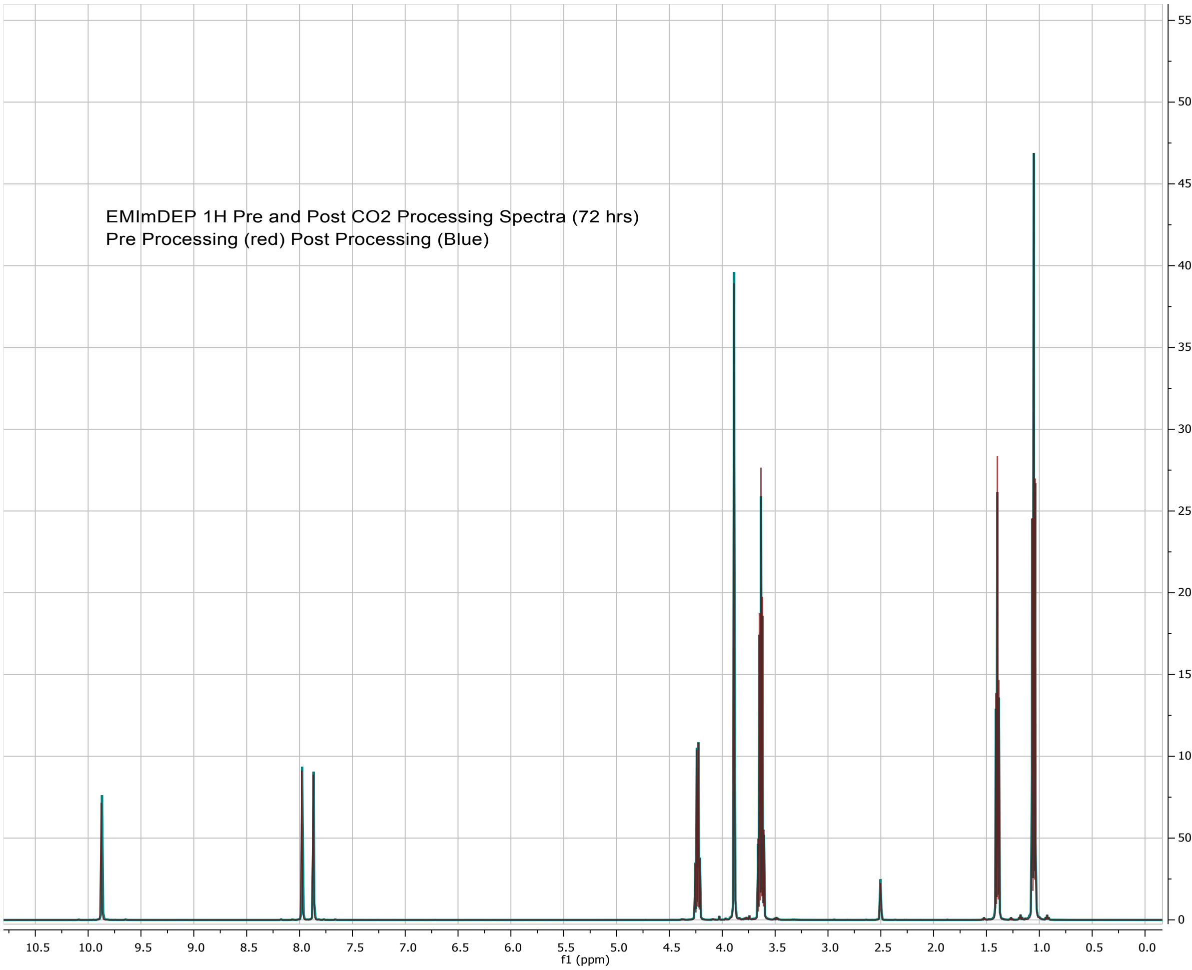

Figure S1: Stacked solution state proton NMR spectra displaying ionic liquid [EMIm][DEP] before (red) and after (blue) 72 hours of CO_2 exposure. Spectra perfectly align and display no formation of new proton resonances indicating IL stability. (DMSO d6 lock solvent)

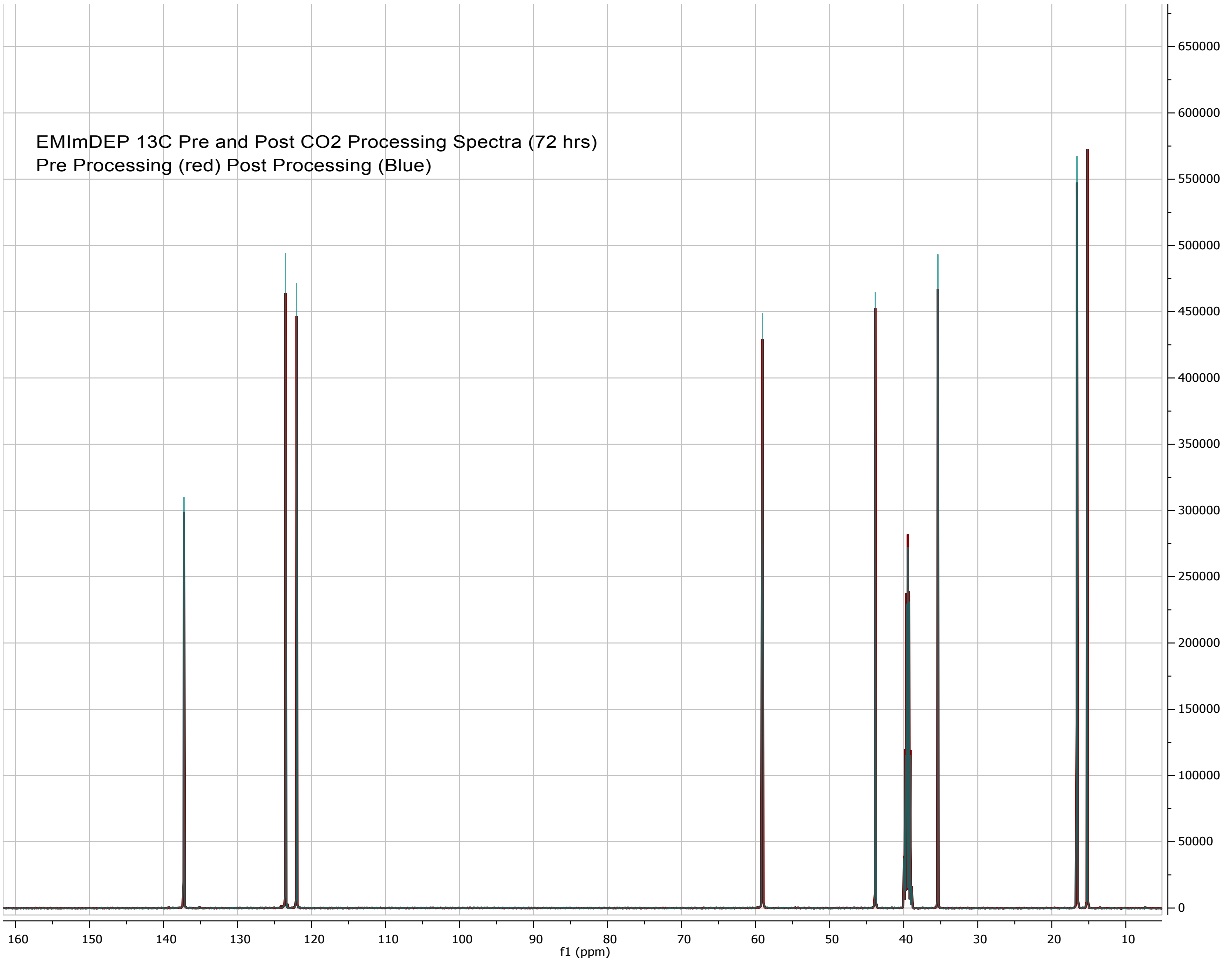

Figure S2: Stacked solution state carbon NMR spectra displaying ionic liquid [EMIm][DEP] before (red) and after (blue) 72 hours of CO_2 exposure. Spectra perfectly align and display no formation of new carbon resonances indicating ionic liquid stability. (DMSO d6 lock solvent)