

ELECTRONIC SUPPLEMENTARY INFORMATION

to accompany

High CO₂ absorption by diamino protic ionic liquids using azolide anions

Tamas Oncsik,^{*a} R. Vijayaraghavan^a and Douglas R. MacFarlane^{*a}

^a*School of Chemistry, Monash University, Clayton Campus, Vic 3800, Australia*

*Email: tamas.oncsik@monash.edu, douglas.macfarlane@monash.edu

Materials:

N,N-dimethylethylenediamine (DMEDA, ≥98.0%), 3-(dimethylamino)-1-propylamine (DMAPA, ≥98.0%), pyrazole (>99.8%), 1,2,4-triazole (>99.0%) were purchased from Sigma Aldrich, while imidazole (>99.5%) was purchased from Merck. They were all used without further purification.

Synthesis and characterisation of the different ionic liquids:

In a typical synthesis, the corresponding amounts of diamine and azole were mixed in a glass vial. Each mixture was sonicated at room temperature until complete dissolution of the azole (for about 10 minutes) resulting in a homogenous liquid. The products were characterised before testing them for CO₂ uptake.

An Anton Paar density meter (model DMA 5000) was used to measure the density of the ionic liquids between 25 °C to 50 °C.

An Anton Paar microviscometer (model Lovis 2000 M) was used to measure the viscosity of the ionic liquids between 25 °C to 50 °C.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC 1 STARE System over a range of 25 – 350 °C under N₂ (30 mL/min), at a heating rate of 10 °C/min.

AC impedance spectroscopy with a frequency ranging from 0.1 Hz to 10 MHz using a 2-electrode Pt wire dip cell was used to measure the conductivity of the different ionic liquids between 25 °C to 50 °C. Before each measurement, a standard KCl solution (0.1 M) was used to calibrate the data and obtain the cell constant. The measurements were performed with a frequency response analyser (Solatron 1296) driven by Solatron impedance measurement software (version 3.2.0).

An ATR-FTIR spectrometer (Perkin Elmer) was used to obtain infrared spectra of the different neat and CO₂-loaded ionic liquids. Each measurement consisted of 64 scans of a resolution of 4 cm⁻¹ in the range of 600–4000 cm⁻¹.

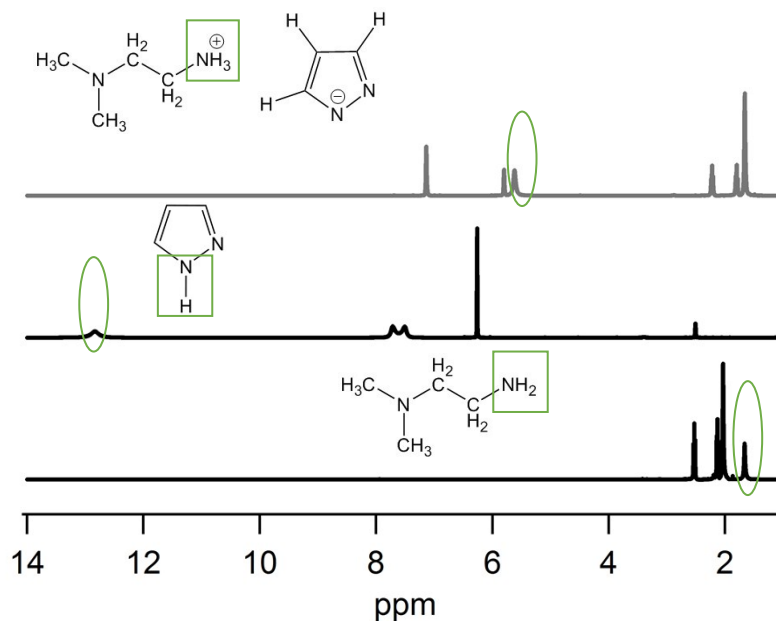
Proton (¹H) and Carbon (¹³C) NMR spectra were obtained on a 400 MHz Bruker DPX-400 spectrometer. All measurements were performed on neat samples at room temperature (25 °C), unless otherwise noted.

CO₂ uptake kinetics:

The measurements were carried out by passing CO₂ through a sample directly in an NMR tube at ambient temperature (22.0±1.0 °C). The purity of the CO₂ was UHP grade, and the flow rate of the gas was set to approximately 50 ml/min. Prior to each measurement, a closed capillary filled with deuterated DMSO was placed into the NMR tube in order to provide a reference for the subsequent spectroscopic analysis. This method made it possible to measure the samples in neat state without using solvents. During the kinetic measurements, the mass increase of the sample was recorded for 60 minutes using an analytical balance. The increment in mass was attributed to the absorbed CO₂.

Absorption/desorption cycles:

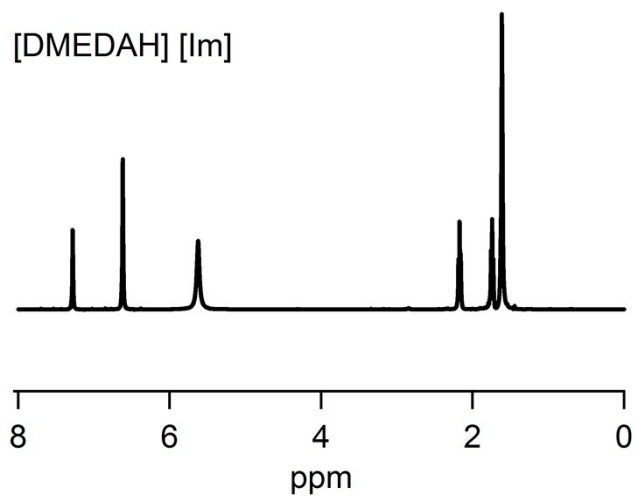
Approximately 0.5 g of [DMAPAH] [Py] was transferred into a glass vial and tested for the recyclability of the absorption process. The absorption was carried out at ambient temperature (22.0±1.0 °C), while the desorption was performed at 50 °C. Both the CO₂ and N₂ were of UHP grade purity. The mass increase/decrease of the sample was recorded using an analytical balance and was attributed to the absorbed/desorbed CO₂.



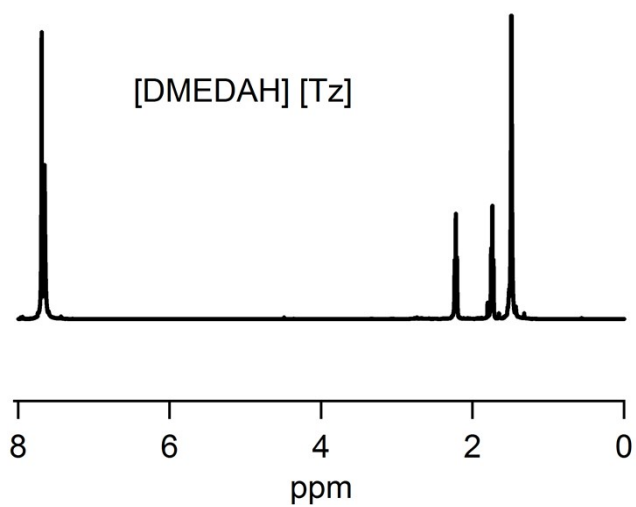
ESI-1 ^1H spectra of the DMEDA as well as pyrazole starting materials and the [DMEDAH] [Py] ionic liquid, the evidence of full protonation is highlighted in green. The different NMR spectra were taken in neat state, except for the pyrazole, which was taken in d^6 -DMSO.

The comparison of the ^1H NMR spectra suggests the completion of this reaction at room temperature in neat ILs. There are two observations that this is happening, and they are the following:

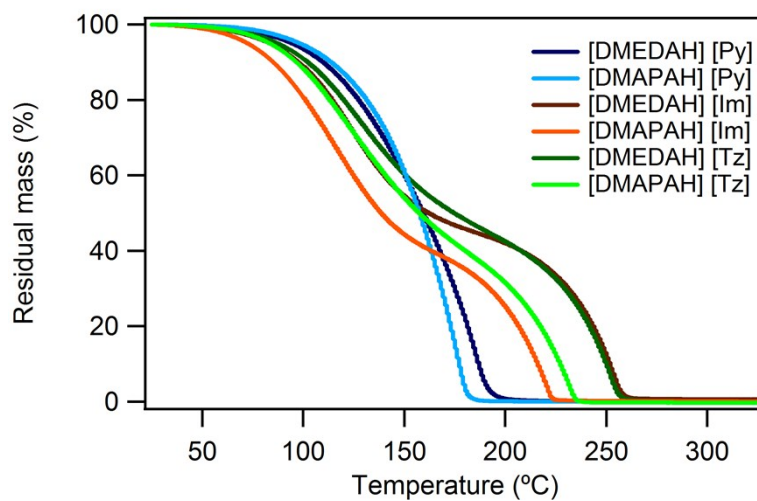
- Comparing the neat DMEDA to the product [DMEDAH] [Py], one can see that the $-\text{NH}_2$ peak is completely missing from the product, whereas a new peak at much higher ppm values appears that can be attributed to the protonated amino group, thus the DMEDA must be protonated.
- Comparing the pyrazole spectra (solid material, measured in d^6 -DMSO) to the neat product, one can see that the $-\text{NH}$ peak around 13 ppm from the protonated azole is completely gone upon the addition of the base. That proton is taken by the amino group of the diamine which is detailed in the previous paragraph. The same phenomena can be observed in the case of imidazole and triazole as well.



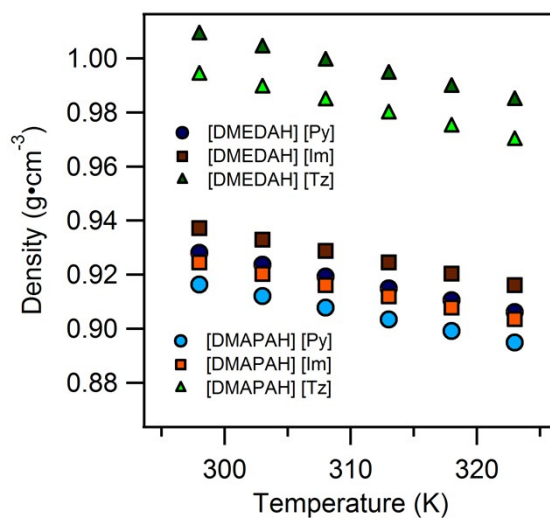
ESI-2 ^1H spectra of the [DMEDAH] [Im] in neat state.



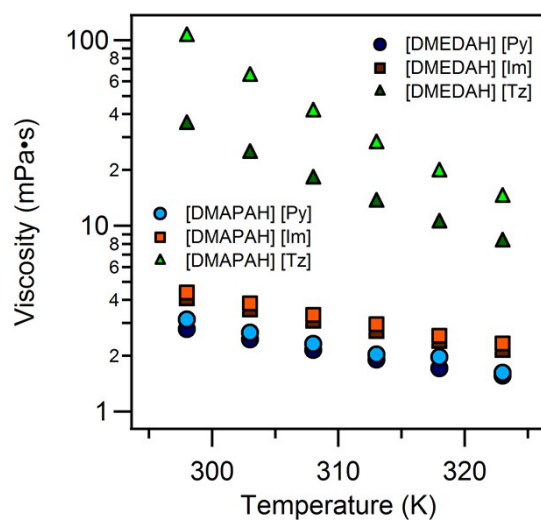
ESI-3 ^1H spectra of the [DMEDAH] [Tz] in neat state.



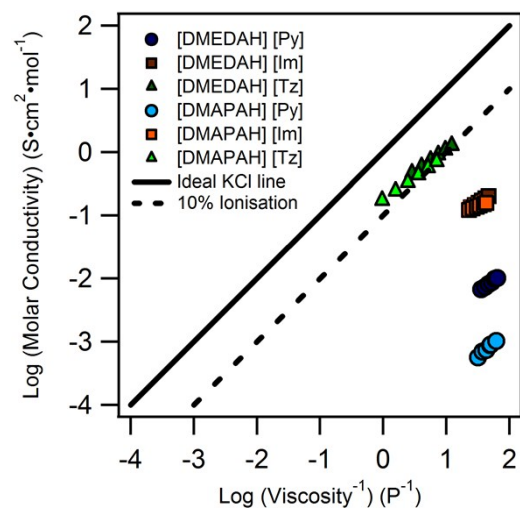
ESI-4 TGA curves of the different neat ionic liquids.



ESI-5 Temperature dependence of the densities of the different ILs investigated.



ESI-6 Temperature dependence of the viscosities of the different ILs investigated.



ESI-7 Walden plot of the different ILs investigated.