



## High CO<sub>2</sub> absorption by diamino protic ionic liquids using azolide anions

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**For the first time, several low-viscosity Diamino Protic Ionic Liquids (DPILs), based on azolides as anions (pyrazolide, imidazolide and triazolide) have been synthesised, characterised and evaluated for CO<sub>2</sub> capture. The results reveal that these ionic liquids rapidly absorb CO<sub>2</sub> to more than 20 %w/w pointing towards equimolar absorption.**

Global warming due to increasing greenhouse gas emissions, such as CO<sub>2</sub>, into the atmosphere, has created significant awareness amongst the scientific community of the need for mechanisms to capture CO<sub>2</sub> reversibly. The conventionally used amine based technology has several issues, including loss of amine in the regeneration process, as well as corroding the tanks and inserts of the equipment. The process is also energy intensive.<sup>1-3</sup> In the last few decades, functionalised and task specific aprotic ionic liquids have been investigated for CO<sub>2</sub> capture and the molar CO<sub>2</sub> uptake of these ILs was found to be around the chemical limit of 0.5 mol/mol imposed by carbamate chemistry in many cases; however, on a mass basis, the capture was less than 10 %w/w.<sup>4-6</sup> There have been several approaches reported in the literature to increase this limit and one such approach is to use multi-amine functionalised ILs. For example, when amine and lysine functionalised groups were introduced into an imidazole based ionic liquid more than 1 mole of CO<sub>2</sub>/mole of IL was obtained.<sup>7</sup> Wang et al demonstrated that  $\pi$  conjugation to the anion of the functionalised IL resulted in excellent absorption of CO<sub>2</sub>.<sup>8</sup> Another approach was to introduce amino groups into a basic phenolic anion to obtain a series of amino functionalised anion ILs in which CO<sub>2</sub> reacts with the amino group through intramolecular proton transfer reactions, thereby improving the absorption capacity.<sup>9</sup> There were also studies on the uptake of CO<sub>2</sub> by employing mixtures (combinations of IL, water and amines) with certain degrees of success.<sup>10, 11</sup>

Recently, protic ionic liquids (PILs) have attracted the attention of researchers, in contrast to conventional aprotic ionic liquids, as they are relatively cheap, easy to synthesise with tuneable physical properties<sup>12-14</sup> and have potential for use in many applications<sup>15-17</sup> including CO<sub>2</sub> capture.<sup>18-20</sup> It was found that cyano-group containing PILs provided selective absorption of CO<sub>2</sub> from SO<sub>2</sub>.<sup>21</sup> Recently our group investigated diamino protic ionic liquids (DPILs) for CO<sub>2</sub> capture.<sup>22</sup> DPILs based on the formate anion resulted in significant CO<sub>2</sub> uptake (around 12 %w/w) coupled with low energy of desorption, in contrast to the conventional MEA process.<sup>23</sup> One of the advantages of the diamines is that they tend to produce lower volatility of the IL. Studies were also made of base-rich versions of the DPILs, while at the same time the effects of diluents such as amines and water were also investigated with these DPILs.<sup>24</sup> The main issue with DPILs is their potential volatility. In order to alleviate the volatility problem, resulting mainly from the smaller carboxylate anions (eg formate), an attempt has been made in this study to replace with thermally more stable azolide anions. Secondly, by avoiding O-containing IL constituents one might expect lower viscosity due to a weaker H-bonding network of the resulting ILs.

Azolide anions have been investigated by Wang et al with quaternary phosphonium cations to obtain aprotic ILs with tuneable physio-chemical properties and these ILs also show good CO<sub>2</sub> absorption capacities.<sup>25</sup> The authors have shown that the stability of the ILs, the enthalpy of absorption, and absorption capacity can be easily tuned by the basicity of the ILs. The intrinsic acidity of the hydrogen at the C-2 position of the imidazolium cation was utilised in combination with an organic superbase to achieve equimolar capture of CO<sub>2</sub>.<sup>26</sup> The influence on CO<sub>2</sub> capture of the alkalinity of the super-base (1,5-diazabicyclo[4.3.0]non-5-enium, DBNH and 1,8-diazabicyclo[5,4,0]undec-7-enium, DBUH) derived cations, in PILs based on azolide anions, has also been investigated; this work showed that the CO<sub>2</sub> absorption involves a mechanism with CO<sub>2</sub> reacting with the azolide anions.<sup>27</sup> Since these superbases are expensive, heavy and the resulting ILs were

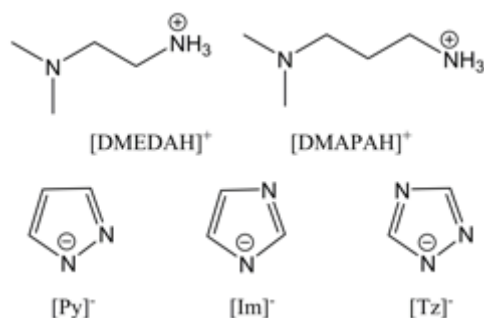
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viscous, our studies are focussed on reducing the cost, viscosity and improving the CO<sub>2</sub> uptake on a w/w basis.

Accordingly in this study, DPILs based on DMEDA (N,N-dimethylethylenediamine) and DMAPA ((3-dimethylamino)-1-propylamine) diamines have been studied and to the best of our knowledge these amines have not been used previously in combination with azoles for CO<sub>2</sub> uptake. The chemical structures of the ionic liquids used in the study are given in **Scheme 1**.

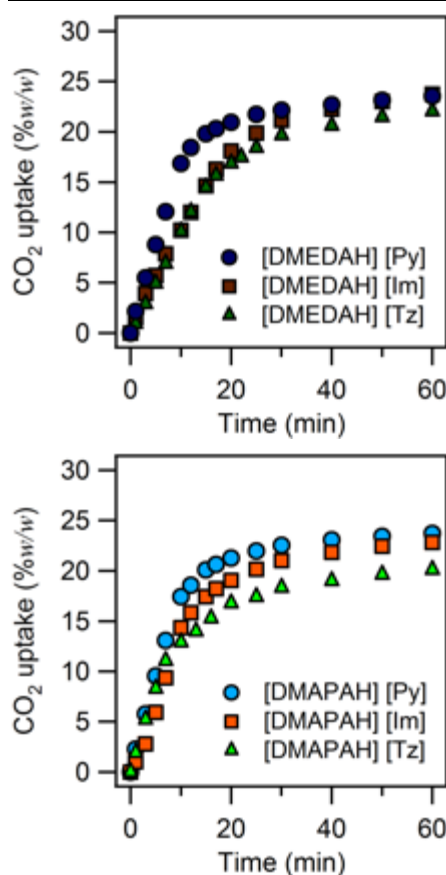


**Scheme 1** Chemical structure of IL constituents in this study.

A series of azolide ILs, based on DMEDAH and DMAPAH cations, were made by sonicating the mixture of the corresponding azoles (pyrazole, imidazole and 1,2,4-triazole) with DMEDA and DMAPA for 10 minutes at room temperature to obtain a homogenous and low viscosity liquid. The ILs were characterised by Electrospray Mass Spectroscopy (ESI-MS), <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, density and viscosity. Full details of experimental methods are presented in the Electronic Supplementary Information. The ESI-MS, as well as the <sup>1</sup>H NMR measurements, showed the formation of the azolides, indicating that the protons from the azoles were completely transferred to the amine in each case. An example is shown in figure ESI-1. It is clear from figures ESI-2 and ESI-3 figures that the density of the pyrazolides and imidazolides of DMEDAH and DMAPAH are lower (ranging between 0.91-0.94 g/cm<sup>3</sup>) and less viscous (1-5 mPa.s) in contrast to the corresponding triazolide salts, between 25-50 °C. This is an important aspect for CO<sub>2</sub> capture as less viscous ionic liquids are preferred for higher absorption rates.<sup>25</sup> Conductivity measurements were carried out at these temperatures to construct Walden plots in order to assess the ionicity of the ILs obtained.<sup>28</sup> The Walden plot is shown in figure ESI-4 revealing that the triazolide-based ILs show fairly good ionicity, while the imidazolide and pyrazolide ILs are poorly ionised. Considering that the <sup>1</sup>H NMR spectra of the different ILs indicate fully protonated amines, the low conductivity of the diazole containing ILs can only be explained by ion-pair formation. The formation of ion-pairs in the diazole-based ILs also produces very low viscosity.

The ILs were then investigated for CO<sub>2</sub> capture and the kinetic profiles of the CO<sub>2</sub> uptake (%w/w) in the DMEDAH and DMAPAH azolides are respectively given in **Fig. 1**. It can be seen that the trends appear to be similar for both DMEDAH and DMAPAH ionic liquids, with the imidazolides and triazolides behaving identically at the initial stages of the

absorption (levelling off around 20 %w/w in about 30 minutes), whereas the DMEDAH and DMAPAH pyrazolides have slightly higher absorption rates within 30 minutes. It is also interesting to note that, in spite of the slightly higher viscosity of DMEDAH and DMAPAH triazolides (in contrast to pyrazolides and imidazolides), the absorption behaviour appears to be only slightly affected in the kinetic measurements. The different absorption capacity values (after 30min) and their comparison with some literature data are summarised in **Table 1**. It can be seen that despite the equimolar uptake of the aprotic phosphonium-based ILs, the mass-uptake values are lower than those presented in this study, due to the much higher molar masses of these ILs. The superbase-containing IL shows similar capacities, however, the high price of the starting material could be expected to limit its applicability.



**Fig. 1** CO<sub>2</sub> uptake kinetics of the different ILs. The CO<sub>2</sub> absorption was carried out at RT (22.0±1.0 °C) and 1 bar.

**Table 1** CO<sub>2</sub> absorption capacities of the different ILs investigated and their comparison with the most relevant literature data.

Ionic Liquid	M <sub>w</sub>	n <sub>CO<sub>2</sub></sub> /n <sub>IL</sub>	%w/w (±5%)	t (min)
[DMEDAH] [Py]	156.23	0.79	22.2	30
[DMEDAH] [Im]	156.23	0.75	21.2	30
[DMEDAH] [Tz]	157.22	0.70	19.7	30
[DMAPAH] [Py]	170.26	0.87	22.6	30
[DMAPAH] [Im]	170.26	0.81	21.0	30
[DMAPAH] [Tz]	171.25	0.71	18.3	30
[P <sub>66614</sub> ] [Pyr] <sup>25</sup>	550.92	1.02	8.2	20
[P <sub>66614</sub> ] [Im] <sup>25</sup>	550.92	1.00	8.0	20

[P <sub>66614</sub> ] [Tz] <sup>25</sup>	551.91	0.95	7.6	20
[DBNH] [Pyr] <sup>27</sup>	192.26	0.87	19.9	30

In order to understand the mechanistic aspects of CO<sub>2</sub> capture by the azolide based ILs, the loaded samples were characterised by FT-IR and <sup>13</sup>C NMR spectroscopy. Typical FT-IR spectra of [DMAPAH] [Py] with different loadings of CO<sub>2</sub> are shown in Fig. 3 (a).

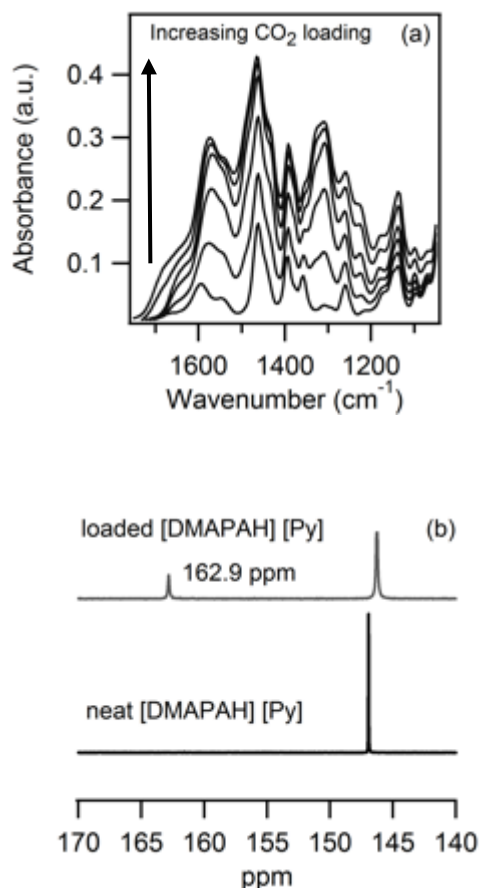


Fig. 2 (a) FT-IR spectra of [DMAPAH] [Py] with different CO<sub>2</sub> loading; (b) NMR spectra of neat and loaded (17.5 %w/w CO<sub>2</sub>) [DMAPAH] [Py].

The figure indicates that the mechanism of the CO<sub>2</sub> absorption is the well-known carbamate formation via the basic nitrogen of the IL, based on the following evidence:

(i) the increasing characteristic peak at 1670 cm<sup>-1</sup> can be attributed to the stretching vibration of the C=O in the carbamate. Considering the structure of the IL, this carbamate could form on both IL constituent ions, however, the increasing peak between 1340 and 1270 cm<sup>-1</sup> suggests that the deprotonated azolide-N is the one involved in the capture. This peak has already been attributed in the literature to the C-N carbamate bond on the azolide.<sup>29</sup>

(ii) the formation of single carbamate peak in the <sup>13</sup>C NMR of the loaded sample (Fig. 3 (b)). It is clear from the figure that the neat IL has no peak in the vicinity of 163 ppm, whereas in the loaded sample there was a clear peak indicating the formation of carbamate salt. A peak at 147 ppm in the neat sample is slightly shifted to 146 ppm and this is usually expected in the loaded sample. We anticipated potentially

more than one carbamate peak in the loaded sample (one from carbamate on the cation and another from carbamate on the anion) but could see only one. We further investigated this by analysing the <sup>13</sup>C NMR of different loadings from very low to high loading (data not shown here) and in all these samples we have observed only one carbamate peak at 163 ppm. This observation is consistent with the growing FT-IR peak at (1340-1270 cm<sup>-1</sup>) in which the deprotonated nitrogen of the anion is involved in the carbamate formation, while the amine functionalities of the cation seem to be inert with respect to the absorption.

The proposed mechanism for the CO<sub>2</sub> uptake is summarised in Fig. 3 with the example of [DMEDAH] [Tz].

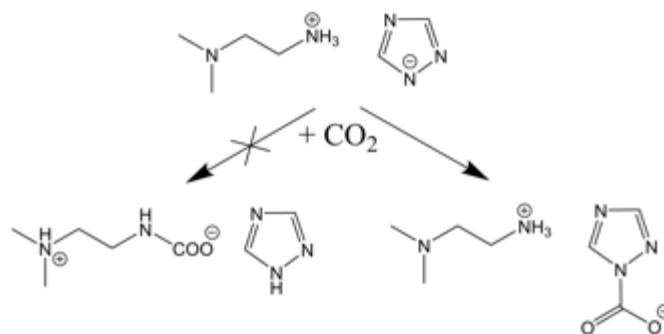


Fig. 3 The proposed mechanism for CO<sub>2</sub> absorption by the ILs investigated, with the example of [DMEDAH] [Tz].

In order to investigate the recyclability of the ILs, absorption/desorption cycles were performed with [DMAPAH] [Py]. It can be seen in Fig. 4 that the captured CO<sub>2</sub> can be easily almost completely released upon slight heating and flushing with N<sub>2</sub>, however the desorption takes longer than loading under the given conditions.

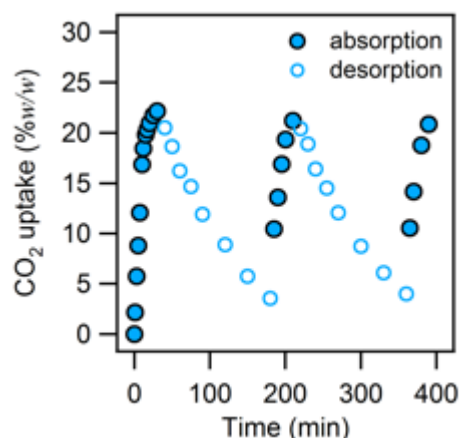


Fig. 4 Absorption/desorption cycles using [DMAPAH] [Py]. CO<sub>2</sub> absorption was performed at RT (22.0±1.0 °C) and 1 bar, while the desorption was carried out at 50 °C under N<sub>2</sub> and 1 bar.

In summary, we have successfully synthesised, characterised and evaluated azolide ionic liquids based on DMEDAH and DMAPAH cations for CO<sub>2</sub> capture. The kinetic studies show

that these ILs have the tendency to rapidly absorb CO<sub>2</sub> with the molar uptake approaching unity. The FT-IR and <sup>13</sup>C NMR studies indicate that the mechanism is via the carbamate formation occurring at the deprotonated azolide-N.

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## Conflicts of interest

There are no conflicts to declare.

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