

## **Sustainable Chemistry: Reversible reaction of CO<sub>2</sub> with amines**

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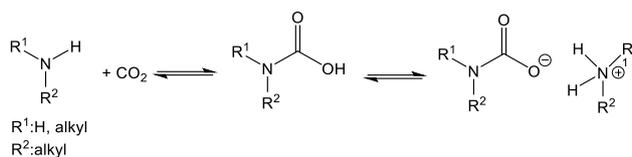
The reaction of primary and secondary amines with CO<sub>2</sub> has been successfully leveraged to develop sustainable processes. In this article, we review specific examples that use the reversible reaction of CO<sub>2</sub> with amines to synergistically enhance reaction and recovery of the products. The three cases of interest highlighted herein are: (i) reversible protection of amines, (ii) reversible ionic liquids for CO<sub>2</sub> capture and chemical transformations, and (iii) reversible gels of ethylene diamine. These examples demonstrate that the reversible reaction of amines with CO<sub>2</sub> is one of the tools in the sustainable technology's toolbox.

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### **Introduction**

The word “sustainable” is defined as “able to continue for a long time”. Within this operational context therefore, “sustainability” must encompass economic, social and environmental aspects of human society. Understanding the global impact of human activities, organizations, and processes (chemicals and others) can promote positive outcomes and minimize negative effect for generations to come. From a chemical processes standpoint, many research activities have aimed at devising innovative approaches that, for example, utilize renewable resources (avoiding petroleum-based feedstock), minimize waste production, recycle rare metals like palladium, and control CO<sub>2</sub> emissions. It is unrealistic to think that one universal solution can effectively address the breadth of the challenges that our society offers. In fact, it is more likely that a toolbox of innovative solutions that are, or can be, tailored to specific challenges will emerge. Over

the past fifteen years, our research group has worked on developing sustainable chemicals and chemical processes. These include environmentally benign tunable solvents (supercritical fluids<sup>[1]</sup>, near critical water<sup>[2]</sup>, CO<sub>2</sub>-gas expanded liquids<sup>[3]</sup>) and smart solvents<sup>[4]</sup> (reversible ionic liquids<sup>[5]</sup>, DMSO substitutes<sup>[6]</sup>). Interestingly, the reaction of amine functionalities with CO<sub>2</sub> has proven to be a cornerstone reaction in the development of some of those sustainable processes. In this personal account, we selected examples that specifically illustrate how one can utilize the reversible reaction of CO<sub>2</sub> with amines to develop sustainable chemical processes. Specifically, we will review: (i) reversible protection of amines, (ii) reversible ionic liquids for CO<sub>2</sub> capture and chemical transformations, and (iii) reversible gels of ethylene diamine. We will conclude with a discussion on the advantages and limitations of the reported strategies.



**Figure 1.** Equilibrium governed reaction of primary and secondary amines to form the carbamic acid and carbamate/ammonium ionic pair.

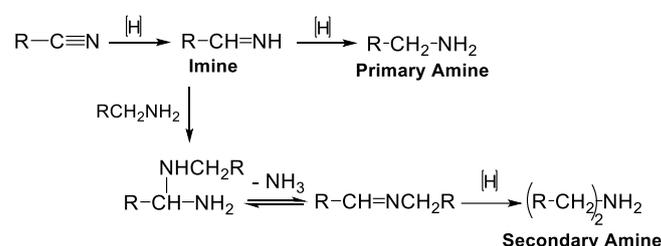
Primary and secondary amines can react with  $\text{CO}_2$  to form carbamic acids and/or ammonium carbamates (**Figure 1**)<sup>[7]</sup>. This reaction has been extensively employed for  $\text{CO}_2$  separation from gases.<sup>[8]</sup> The reaction can be easily tuned by changing (i) the structure of the amine, (ii) the pressure of  $\text{CO}_2$ , (iii) the temperature, or (iv) the absence or presence of solvent. The beauty of the  $\text{CO}_2$ -amine reaction is that it can be reversed thermally under relatively mild conditions—a key to developing reversible or “smart” processes. Primary amines react rapidly with  $\text{CO}_2$ , and as a result, the reversible reaction to recover the “free” amine and  $\text{CO}_2$  would usually require more energy. The nucleophilicity of the nitrogen atom toward  $\text{CO}_2$  can be controlled by increasing steric hindrance on alpha position of the primary amine or by using a secondary amine. With an appropriate balance, the forward reaction with  $\text{CO}_2$  is still rapid but allows for a more controlled reactivity and an easier reversal reaction—such scenarios are suitable for carbon capture and sequestration applications for example.

## Results and discussion

### Reversible Protecting Strategies

Protection/deprotection sequences enable reaction at specific sites without interference or competitive reactions at other sites in the same molecule. Intrinsically, protecting groups must be introduced and subsequently removed. In order for this scheme to be useful, the yields associated with the protection and subsequent deprotection must be near quantitative. In the

specific case of amine groups, the reversible reaction of  $\text{CO}_2$  with primary and secondary amines offers unique opportunities for in-situ, reversible protection. This approach would be superior to the traditional “linear” protection/deprotection sequence since it minimizes the number of steps in the synthetic sequence as well as the overall waste signature. Several reports have demonstrated the viability and simplicity of these strategies.<sup>[9]</sup> For example, both the homogeneous and heterogeneous catalyzed hydrogenation of nitriles usually produces low yields and selectivity. This is the result of the side reaction of the product, a primary amine, with the imine intermediate (**Figure 2**).



**Figure 2.** Hydrogenation benzonitrile ( $\text{R}=\text{Ph}-\text{CH}_2$ ).

To optimize the yield of the desired primary amine, it can be trapped in-situ upon reaction with acetic anhydride or di-*tert*-butyl dicarbonate to form the N-acetyl and N-Boc protected amine, respectively. This approach successfully increases yields as it suppresses further reaction of the primary amine product. However, it also requires a subsequent step to remove the newly introduced protecting group. Xie *et al.* have reported the use  $\text{CO}_2$ -expanded liquids (GXLs) as solvents for this reduction process.<sup>[10]</sup> In this report, advantage is taken of the fact that  $\text{CO}_2$  readily dissolves in a wide variety of polar organic solvent. These systems are termed “ $\text{CO}_2$ -expanded liquids” and are simply mixtures of polar organic solvent and  $\text{CO}_2$ . Practically, the pressure of  $\text{CO}_2$  can be adjusted to manipulate the amount (molar fraction) of  $\text{CO}_2$  dissolved in the organic solvent. When the reduction of nitrile is conducted in  $\text{CO}_2$ -expanded liquids, the primary amine product reacts in-situ with the

dissolved CO<sub>2</sub> to form carbamic acid and/or carbamate thus “protecting” the amine from further reaction with the imine intermediate. In contrast with traditional protection strategies such as those utilizing acetyl or Boc, a simple depressurization (or when necessary mild heating) reverses the carbamic acid/carbamate product to the desired primary amine product. This eliminates the need of an additional more complex deprotection step. Specifically in CO<sub>2</sub>-expanded ethanol, the yields of the primary amine reach up to 99 % under homogeneous conditions.

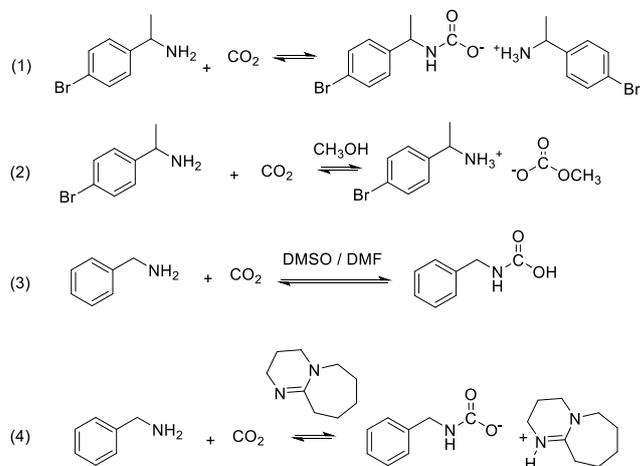
	Protecting agents	Time (hrs)	Secondary amine yield (%)	Primary amine yield (%)
1	without protection	4	96	<0.01
2	acetic anhydride	24	1.6	87
3	di- <i>tert</i> -butyl dicarbonate	24	0.1	99
4	<b>carbon dioxide (30 bar)</b>	<b>24</b>	<b>0.1</b>	<b>98</b>

**Table 1.** Experimental yield of hydrogenation of benzonitrile with sodium borohydride in presence of NiCl<sub>2</sub> in ethanol at 30°C.

The hydrogenation reaction of benzonitrile with sodium borohydride catalyzed by NiCl<sub>2</sub> was conducted in ethanol at 30°C (**Table 1**). The amine yields for both the primary amine (desired) and secondary amide (undesired) was monitored as a function of protecting strategies, i.e. (i) without protection, (ii) in the presence of two equivalents of acetic anhydride (in situ formation of R-NHCOCH<sub>3</sub>, N-Ac), (iii) in presence of two equivalents of di-*tert*-butyldicarbonate (in-situ formation of R-NHCO<sub>2</sub>t-Bu, N-Boc) and (iv) under 30 bar of CO<sub>2</sub> (in-situ CO<sub>2</sub> protection as carbamic acid/carbamate) was conducted. Without protection, the secondary amine (dibenzylamine) is the major product (96%). In contrast, with traditional in-situ protection (N-Ac and N-Boc), selectivity toward the primary amine is reversed to the primary amine, with 87 and 99 % yield, respectively (Entries 2 & 3). The

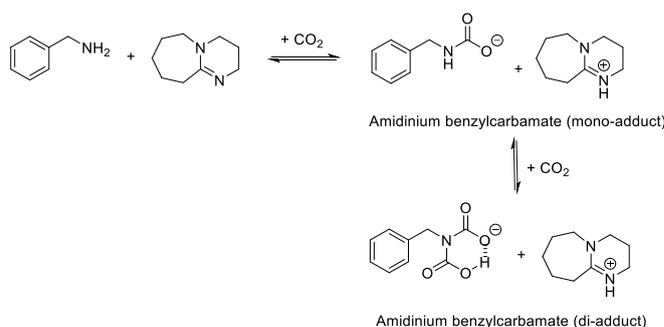
in-situ protection with CO<sub>2</sub> using a GXL shows analogous results to the N-Boc protection, with 98 % yield of primary amine (Entries 4). Unlike Boc strategy, the CO<sub>2</sub>-triggered protection is easily reversed to the free-amine by depressurization and/or mild heating—no additional steps are required.

More recently, Peeters *et al.* demonstrated the successful protection of primary and secondary amines for acylation reaction and Michael additions.<sup>[9b]</sup> Additionally, Ethier *et al.* reported the protection of benzylamines upon reaction with carbon dioxide in various solvents with and without addition of bases.<sup>[9a]</sup> The reaction of the benzyl amines was shown to be highly dependent on the reactions conditions as shown in **Figure 3**. In neat conditions (1) or in polar protic solvents like methanol (2), the ammonium/carbamate ionic pair is principally formed. In polar aprotic solvent like DMSO (3), the carbamic acid become the predominant product.



**Figure 3.** Reaction of benzyl amine derivatives with CO<sub>2</sub> as a function of added solvent and/or base.

In acetonitrile and in the presence of a strong base like DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), benzylamine reacted with one or two moles of CO<sub>2</sub> to form the “mono-adduct” (4) and the “di-adduct” products (**Figure 4**), respectively.



**Figure 4.** Reaction of benzylamine with CO<sub>2</sub> in presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).

The authors report that the reversal reaction (i.e. deprotection) was achieved by applying mild heating (60-70°C) for one hour. Furthermore, the competitive intramolecular *O*-acylation and *N*-acylation of (4-(aminomethyl)phenyl)methanol was successfully demonstrated. The results are summarized in **Table 2**.

Entry	CO <sub>2</sub>	DBU (eq)	Iso-PA (eq) <sup>b</sup>	Time (h)	<i>O</i> -Product <sup>c</sup> (%)	<i>N</i> -Product <sup>c</sup> (%)
1	No	1	1	6	40	60
2	No	1.2	1.7	6	70	100
3	Yes	1	1	6	15	0
4	Yes	1.2	1.7	6	30	0
5 <sup>a</sup>	Yes	1.2	1.7	24	80	0

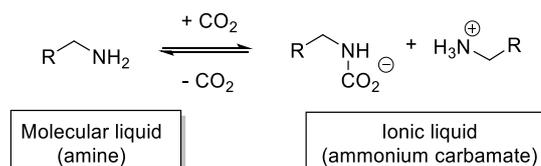
<sup>a</sup> 1 mol % triazole; <sup>b</sup> Isopropenyl acetate; <sup>c</sup> Yield determined by <sup>1</sup>H NMR.

**Table 2.** Experimental conversions of *N*-acylation and *O*-acylation with and without CO<sub>2</sub> protection.

With no protection, both *O*- and *N*-acylations are observed (entries 1 & 2). In contrast, when the amine is first reacted with CO<sub>2</sub>, the *N*-acylation reaction is suppressed. Only *O*-acylation is observed in 80% yield. These results demonstrate the potential applicability of CO<sub>2</sub> as an in-situ, reversible strategy for amines in multi-steps synthesis.

### Reversible ionic liquids for CO<sub>2</sub> capture and chemical transformation

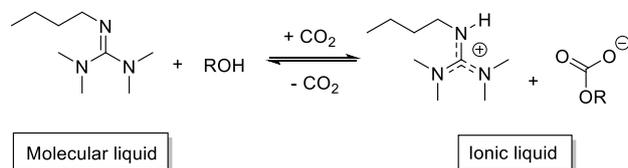
There is an on-going demand in the chemical industry for environmentally friendly and recyclable solvents. Ideally such solvents would enable reactions to occur in high yields under reasonable conditions and provide for effective isolation of product. Additionally, the ability to recycle the solvent would also be of great economic value. Switchable solvents can potentially fulfill this role. The possibility to reversibly “switch” the nature of a solvent (ionic vs. covalent) by controlled manipulation on a molecular level can provide the foundation for economical and sustainable chemical processes. Operationally, the polarity of the solvent can be altered by simply applying a controllable stimulus such as heat. An early example of such reversible or switchable solvent systems is dimethylammonium dimethylamine carbamate, also called Dimcarb. Dimcarb is an ionic liquid that is formed upon reaction of dimethyl amine, a low boiling point liquid (bp 7°C), with CO<sub>2</sub>.<sup>[11]</sup> Remarkably, Dimcarb is a “distillable” ionic liquid. Upon heating the reaction is reversed to yield the gaseous reaction partners, dimethylamine and CO<sub>2</sub>, which spontaneously recombined upon cooling. Reversible ionic, like their traditional ionic liquid analogs, can be designed for specific applications. Unlike traditional ionic liquids however reversible ionic liquid can be switched back and forth from a molecular liquid (non-ionic liquid like an organic amine) to an ionic liquid upon the reaction with CO<sub>2</sub> (**Figure 5**). This unique reversibility was used as the foundation for revisiting industrially relevant processes; this includes CO<sub>2</sub> capture,<sup>[12]</sup> chemical transformations like Claisen-Schmidt reactions and Heck couplings,<sup>[13]</sup> polymerization,<sup>[14]</sup> and crude oil recovery.<sup>[15]</sup>



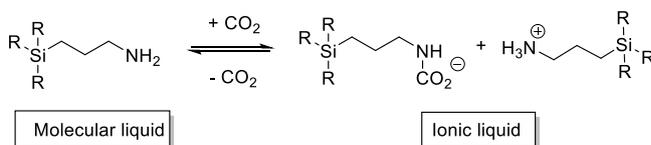
**Figure 5.** Reversible switch from a molecular liquid mixture of amine to the ionic liquid (carbamate-ammonium ion pair) upon addition of CO<sub>2</sub>.

Two type of reversible ionic liquids have been reported (**Figures 6**).<sup>[15a, 16]</sup> One type is termed a “two-component” ionic liquid. An example is the ionic species formed upon mixing equimolar quantities of guanidines or amidines and alcohols and subsequently treating with CO<sub>2</sub>. These “two-component” ionic systems have been used for chemical transformations such as Claisen-Schmidt reactions and Heck couplings,<sup>[13]</sup> polymerization.<sup>[14]</sup>

**Two-component system**



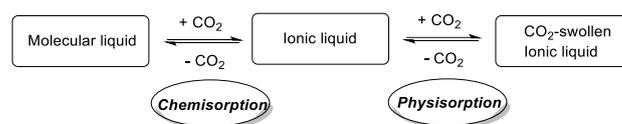
**Single component system**



**Figure 6.** Two-component system composed of mixture of TMBG and alcohol (R--OH) to the ionic liquid [TMBGH]<sup>+</sup>[RCO<sub>3</sub>]<sup>-</sup> upon addition of CO<sub>2</sub> (R= C<sub>1</sub> to C<sub>12</sub>). One-component system using trialkoxy- or trialkylsilylpropylamine) to its corresponding ionic liquid upon addition of CO<sub>2</sub>. (R= OC<sub>1</sub>, OC<sub>2</sub>, C<sub>2</sub> or C<sub>3</sub>.)

The second type is a “single-component” ionic liquid that is based upon silyl-containing amines such as trialkoxy- and trialkylsilylpropylamine (**Figure 6**). It is conjectured that the presence of the silicon is essential to the liquid character of the resulting ionic species. Although, trialkoxysilylpropylamine successfully and reversibly yield ionic liquids upon reaction with CO<sub>2</sub>, the hydrolytic instability of the Si-O bond is a severe limitation to its general use as a reaction solvent. In contrast, trialkylsilylamines do not suffer from such instability and as a result are much preferable for applications like CO<sub>2</sub>-

capture.<sup>[15c]</sup> Traditionally, the amine-based technologies for CO<sub>2</sub> capture are aqueous systems, which suffer from high energy footprint. One of the main factors is the large energy penalty to heat water (due to its high heat capacity) in the CO<sub>2</sub> recovery step. This limitation is eliminated with materials such as reversible ionic liquids than can be operated without water or co-solvent. RevILs can operate neat under both chemisorption and physisorption modes (**Figure 7**).<sup>[17]</sup>



**Figure 7.** Reaction of amine with CO<sub>2</sub> to form ionic liquid (**chemisorption**) followed by dissolution of CO<sub>2</sub> into the newly form ionic liquid (**physisorption**).

The chemisorption results from the selective and reversible reaction with CO<sub>2</sub> to form the carbamate/ammonium based ionic liquid. Chemisorption mode is the primary capture mechanism for low CO<sub>2</sub> pressure applications (<1 bar). The physisorption, especially important for high CO<sub>2</sub> pressure (>20 bar), results from the CO<sub>2</sub> dissolution within ionic liquids (analogous to CO<sub>2</sub> expanded liquids, traditional and task-specific ionic liquids)<sup>[18]</sup> There are several limitation to some of these reversible ionic liquids. At full conversion (i.e. 100% ionic liquid), reversible ionic liquid like traditional ionic liquids tends to exhibit high viscosity; this can be a problematic limitation for large scale processes such as CO<sub>2</sub> capture. As an example, the viscosity of tripropylsilyl propylamine based ionic liquid at full conversion at room temperature is about 4000 cP at 25°C and 1000cP at 40°C. Like traditional ionic liquids the structure of reversible ionic liquids can be modified to alter bulk properties. For instance, by replacing the propyl chain of the silyl group by the hexyl group, the viscosity at 25°C was

decreased by a factor of two. Specifically, trihexylpropylamine at full conversion (100% ionic liquid form) exhibit a viscosity of about 2300cP at 25°C and 700cP at 40°C. In the case of the silylamine-based reversible ionic liquids, it was shown that the influence of the length of the alkyl tether (between the silyl and amine groups) or the position of one or more methyl groups on the silylamine (tether or reactive amine groups) also had significant effect on reaction enthalpy, viscosity, and reversal temperature.<sup>[12a]</sup> However, unlike classical or permanent ionic liquid systems, the viscosity of reversible ionic liquid is a function of the extent of reaction (Figure 8).

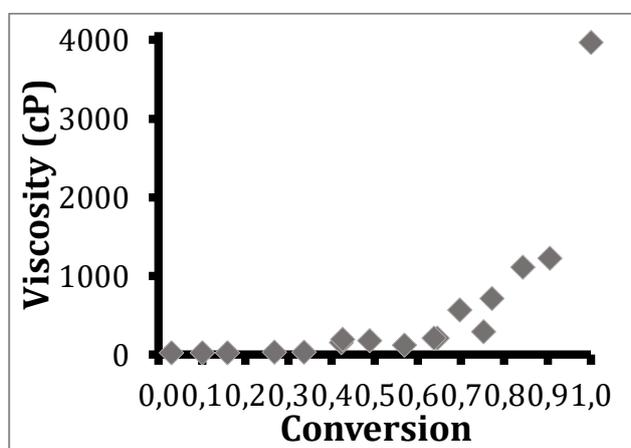


Figure 8. Viscosity as a function of conversion of tri-propylsilylamine and CO<sub>2</sub> at 25°C.

The viscosity of tripropylsilylpropylamine is low (~25 cP) as expected for an organic solvent. As can be seen in Figure 8, the viscosity remain relatively low, below 200cP until ~ 70% conversion. Then, the viscosity starts to increases significantly to about 100cP at 90% conversion, to finally spike to 3970 cP at full conversion. It is believed that up to 70-80 % conversion, the ionic species are dissolved in the un-reacted amine; the unreacted amine is the solvent for the ionic liquid. At high conversions however, the ionic liquid is the predominant species, i.e. the solvent. The unreacted amine is virtually dissolved in the ionic liquid. Unlike classical or permanent ionic

liquid systems, the viscosity of the reversible system can be easily tailored.

### Reversible gels of ethylenediamine

Organogels are a class of materials that result from the self-association of small molecules into supramolecular structures due to ordering from interactions like hydrogen and ionic bonding, van der Waals and  $\pi$ - $\pi$  stacking interactions, solvophobic effects or combinations of these.<sup>[19]</sup> The thermoreversible gelation of solvents like octanol using hydrophobic amines (octyl to octadecylamine) as “latent” gelators has been reported by Weiss *et al.*<sup>[20]</sup> After reaction with CO<sub>2</sub>, gelation occurs resulting from the self-association in a strand type network of the long alkyl chain carbamate salts. Upon heating at, or above, 80°C the liquid state can be restored as the latent gelators is reversed to the amine and CO<sub>2</sub>. The authors showed that the structure of the amines can be altered to tailor the properties of the ammonium carbamate ion pair as latent gelling agents-a reminiscence of the reversible ionic liquid systems.<sup>1</sup> In our laboratory, we have shown that pure ethylenediamine reacted with CO<sub>2</sub> (gaseous or solid dry ice) at room temperature to quickly form a transparent gel (Figure 9).

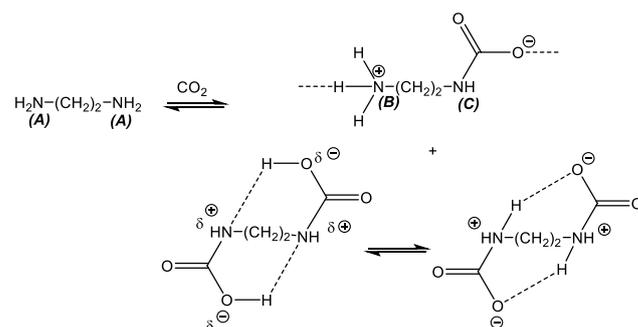
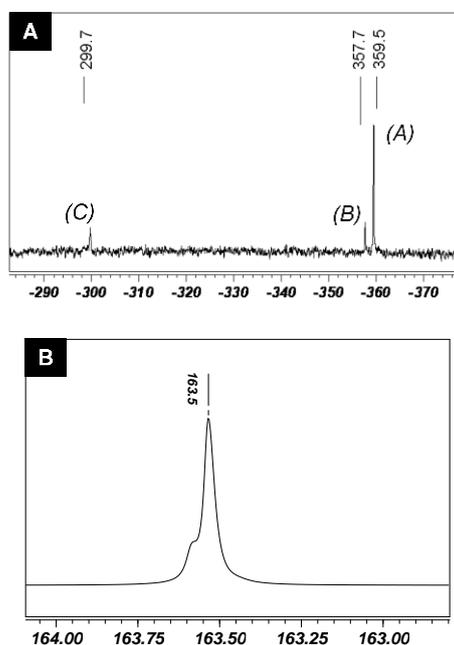


Figure 9. Reaction of ethylenediamine with carbon dioxide to form carbamate corresponding species.

As determined by elemental analyses, the mol ratio of ethylenediamine to CO<sub>2</sub> was consistently 1 to 0.5 within experimental error. The <sup>15</sup>N NMR spectrum of pure ethylenediamine exhibited one peak at -362 ppm indicating two equivalent

nitrogens. In contrast, the  $^{15}\text{N}$  of ethylenediamine- $\text{CO}_2$  gel NMR spectrum exhibited three major peaks (**Figure 10A**). The major peak at -359.5 ppm (A) was attributed to the un-reacted ethylenediamine. The two other peaks at -357.7 (B) and -299.7 (C) ppm were attributed to the new carbamate species (**Figure 9**). From the  $^{13}\text{C}$  spectra, two overlapping peaks could be distinguished at 163.5 ppm (**Figure 10B**), consistent with the new carbamate species. Within the detection limit of natural abundance  $^{15}\text{N}$ , it appears that the formation of the monocarbamate species is favored.



**Figure 10.** A.  $^{15}\text{N}$  (natural abundance) spectrum of the neat ethylenediamine- $\text{CO}_2$  material, B.  $^{13}\text{C}$ -enriched spectrum of the neat ethylenediamine- $\text{CO}_2$  material.

Overall, both NMR studies and the elemental analyses support the presence of two major species: the zwitterion 2-ammonium-ethylcarbamate and the unreacted ethylene diamine. It is conjectured that the 2-ammonium-ethylcarbamate arranges into a framework via cooperative ionic and hydrogen bonds. Ethylenediamine is among the smallest and

simplest “latent” gelators ever reported. Unreacted ethylenediamine is held in the interstices, thus forming gels. Furthermore, the gels can easily revert to the pure components upon addition of solvents (i.e. water, ethyl acetate, etc..) or mild heating.

## Conclusions

The on-going technological challenges require that we continue to develop sustainable solutions to address the ever-reaching scope of challenges of chemical processes. The examples presented here represent just one of several strategies in the sustainable solvent toolbox. For reversible protecting strategies, primary amines are easily reacted with  $\text{CO}_2$  to decreasing the nucleophilicity of the amine with the formation of carbamate species. The simplicity of reversing this process to produce the “free” amine by just simply administering mild heat eliminates the need for a separate deprotection step. The reactivity of the carbamate or carbamic acid protected species must however be considered in light of multi-synthetic sequence. Additionally, it has been demonstrated that reversible ionic liquids allow for an energy-conscious, solvent free effective  $\text{CO}_2$  capture alternative or chemical transformations. This advantage arises from the ability to use these reversible systems neat (no aqueous systems), as the presence of large amount of water can lead to the formation of carbonate species, which are more difficult to reverse under mild conditions than their carbamate analog. Finally, the last example showed ethylene diamine as one of the smallest, reversible gelator. It spontaneously self-assemble upon reaction of  $\text{CO}_2$ . This concept can easily be extended to other molecules such as simple hydrazine to control, for example, vapor pressure and viscosity. The reversibility allow that upon small heat the gelling agent can easily be reversed to restore liquid state. These

applications are meant to illustrate that the flexibility and versatility of equilibrium governed reactions such as the reaction of amines with CO<sub>2</sub> can prove to be an important resource in developing sustainable chemical processes.

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