

# Aqueous Carboxylic Acid-Based Solutions for CO<sub>2</sub> Capture

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## ABSTRACT

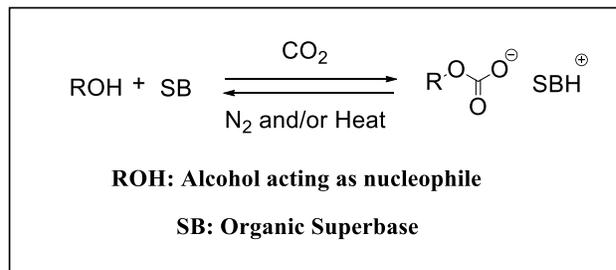
This report, describes the concept of multifunctionalized-carboxylate-based Task-Specific Ionic Liquid (TSIL) in combination with controlled quantity of water, in order to capture CO<sub>2</sub>. Different examples of TSILs were prepared centred on a acid-base reaction between formic acid, di-, tri-, tetra- and multifunctionalized carboxylic acids in combination with the proper number of equivalents of an organic superbase, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). The TSILs preparation method sustainability is centred on the atom economy of the reaction and use of ethanol as solvent. The use of one of these Ionic Liquids is highlighted in this work, namely the DBU-based salt of Aspartic acid: [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>]. An aqueous solution of this salt was prepared and tested for carbon dioxide capture. CO<sub>2</sub> uptake in wt% was obtained and evaluation of reactional mixture by NMR and FTIR techniques was carried out.

**Keywords:** carbon dioxide capture, ionic liquid, organic superbase, water, multifunctionalized-carboxylates.

## 1 INTRODUCTION

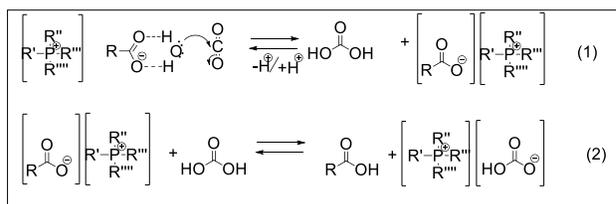
Considering the present society standards of living and associated energetic consumption requirements depending on fossil fuels, is highly sought efficient systems that mitigate anthropogenic carbon dioxide footprint. The benchmark systems for CO<sub>2</sub> capture, available in the market for more than 60 years, are based on aqueous solutions of monoethanolamine and the main drawbacks consist in solvent loss, degradation, high energy demand and relatively poor performance in carbon dioxide capture. [1] Considering this framework, alternative Ionic Liquid-based technologies (IL) were developed [2-7]. The negligible volatility and the possibility to incorporate specific functionalities able to react with CO<sub>2</sub> are advantages to have in account. In opposition, the high price associated and the requirement of multiple synthetic steps, convert ILs in technologies difficult to implement at large scale.

In a different perspective, the concept of reversible ionic liquid using CO<sub>2</sub> as element of reversibility, was created by Jessop et al [8] in 2005. On that report an alcohol, in the presence of an organic superbase, reacted with CO<sub>2</sub>, leading to carbonate-based salt. The system could revert back to non-ionic state after introduction of N<sub>2</sub> as displacement gas, with the consequent release of CO<sub>2</sub> (Fig. 1).



**Figure 1:** Concept of reversible ionic liquid using CO<sub>2</sub> as element of reversibility.

Later on, different aspects of the same paradigm were developed such as the use of other gases (SO<sub>2</sub>, COS and CS<sub>2</sub>), as elements of reversibility [9], the test of other nucleophiles, such as amines [10,11], amino-acids [12], amino-esters [13], amino-alcohols [14], and saccharide-based structures, [15, 16], comparative study of performance of different organic superbases, and presence of multiple functionalities able to react with CO<sub>2</sub>. Some of these reversible systems lead to high CO<sub>2</sub> uptakes (wt%). [16] In the same context, Anderson et. al, [17] developed systems centred on non-protic carboxylate-based ionic liquids with high molecular weight. The carboxylate functionality activate water molecules promoting an amplified reaction with CO<sub>2</sub> leading to bicarbonate based salts and the protonation of the carboxylate (Fig. 2).



**Figure 2:** Concept of carboxylate-based activation of water molecules for CO<sub>2</sub> capture, using a TSIL.

In the present work we combine three different concepts:

- 1) Reversible IL, and associated activation of a nucleophile by an organic superbase to react with CO<sub>2</sub>.
- 2) Use of carboxylate based TSILs for activation of water molecules to act as nucleophiles to react with the same gas.

3) Use of multiple functionalities in the same molecule able to activate water in order to react with CO<sub>2</sub>.

Considering these aspects we developed novel carboxylate based TSILs, result from an acid-base reaction between the proper number of equivalents of an organic superbase (DBU) and multifunctionalized carboxylic acids. Parsimonious quantities of water were added in order to balance the negative effects of low solubility of CO<sub>2</sub> in this solvent with the promoting effect of reduced viscosity (optimized diffusion of CO<sub>2</sub> in the reaction media) and, of course, the required amount for reaction with CO<sub>2</sub>. [17]

Different carboxylic acid-based compounds mono-, di-, tri-, tetra- and multifunctionalized were used to prepare the respective TSIL's.

As proof of concept, is presented in this report the prepararion of the salt of Aspartic acid, [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>], followed by the mixture of the salt with water, and finally, the reaction of the mixture with CO<sub>2</sub>. At all stages a complete spectral characterization was carried out.

## 2 EXPERIMENTAL SECTION

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), > 98%, was provided by TCI, differently, L-Aspartic acid (≥ 99%) was produced by Sigma Aldrich, similarly as ethanol (≥ 99.8%). Distilled water was used to prepare the mixture tested on CO<sub>2</sub> capture.

The prepared compounds and reactional mixtures were characterized by <sup>1</sup>H, <sup>13</sup>C NMR, HMBC and HSQC recorded on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in parts per million from a tetramethylsilane reference. IR spectra were recorded on a Perkin Elmer FTIR Spectrometer, Spectrum 1000. The samples were prepared in a KBr matrix.

### 2.1 [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>]

DBU (2 g. – 2 eq.) dissolved in 5 mL. of ethanol was added slowly, to a stirred mixture of aspartic acid (0.865 g. – 1 eq.) suspended in the same solvent (5 mL.). The reactional mixture was stirred under ambient temperature and pressure during 21 h. After completion of reaction the solvent was evaporated, and the remaining mixture submitted to high vacuum. The product is a yellow viscous gel, obtained with a yield of 95.1%. <sup>1</sup>H-NMR (400 MHz, d<sub>6</sub>-DMSO): δ: 1.58-1.64 (m, 12H), 1.82 (quint, J = 4 Hz, 4

H), 2.00 (dd, J<sub>1</sub> = 16 Hz, J<sub>2</sub> = 8Hz, 1H), 2.35 (dd, J<sub>1</sub> = 16 Hz, J<sub>2</sub> = 4 Hz, 1H), 2.63 (m, 4H), 3.20 (t, J = 6 Hz, 4H), 3.32 (m, 1H), 3.37 (t, J = 6 Hz, 4H), 3.43 (m, 4H), 5.25 (bs, 12H) ppm. <sup>13</sup>C-NMR (100 MHz, d<sub>6</sub>-DMSO): δ: 19.94, 24.22, 26.68, 28.58, 32.34, 39.02, 47.75, 52.78, 52.90, 163.96, 174.25, 175.05 ppm. FTIR (KBr): 3423, 3128, 2938, 2861, 2806, 2688, 1649, 1587, 1505, 1472, 1448, 1397, 1359, 1325, 1270, 1243, 1208, 1160, 1107, 1091, 996, 913, 886, 682, 668, 531 cm<sup>-1</sup>.

### 2.2 [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>] + H<sub>2</sub>O

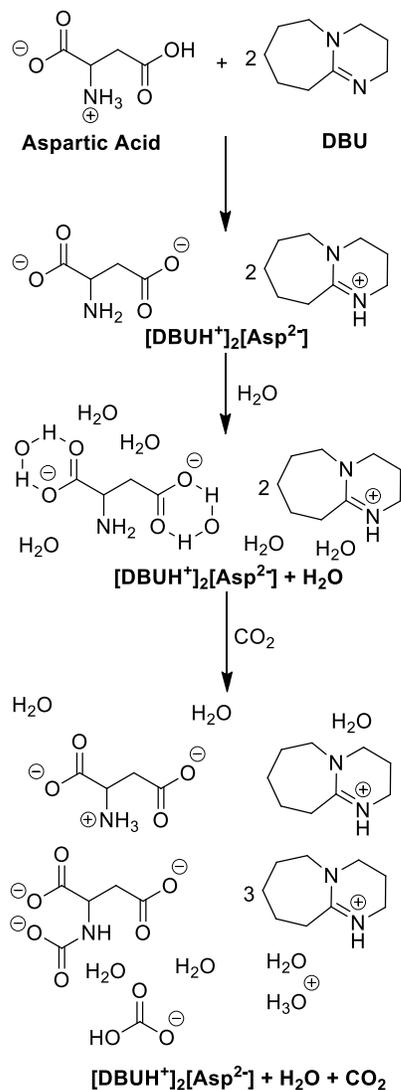
In order to carry out the reaction with CO<sub>2</sub>, 0.32 g. of water was added to 1.00 g. of [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>], under stirring. The mixture was characterized by the conventional techniques: <sup>1</sup>H-NMR (400 MHz, d<sub>6</sub>-DMSO): δ: 1.57-1.63 (m, 12H), 1.82 (quint, J = 6 Hz, 4 H), 2.04 (dd, J<sub>1</sub> = 16 Hz, J<sub>2</sub> = 8Hz, 1H), 2.34 (dd, J<sub>1</sub> = 16 Hz, J<sub>2</sub> = 4 Hz, 1H), 2.58-2.60 (m, 4H), 3.19 (t, J = 6 Hz, 4H), 3.32 (m, 1H), 3.37 (t, J = 6 Hz, 4H), 3.41-3.43 (m, 4H), 4.20 (bs, 26 H) ppm. <sup>13</sup>C-NMR (100 MHz, d<sub>6</sub>-DMSO): δ: 19.97, 24.22, 26.69, 28.58, 28.89, 32.45, 35.95, 47.74, 52.77, 55.12, 163.89, 173.23, 176.87 ppm. FTIR (KBr): 3425, 3238, 3122, 2970, 2937, 2863, 1648, 1589, 1471, 1454, 1399, 1325, 1271, 1207, 1140, 1107, 1091, 997, 985, 968, 901, 846, 826, 801, 744, 675, 660, 617, 606, 580, 533 cm<sup>-1</sup>.

### 2.3 [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>] + H<sub>2</sub>O + CO<sub>2</sub>

The mixture [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>] + H<sub>2</sub>O, prepared in the previous step, was placed in a high pressure reactor, such system was weighted previously to the reaction. Afterwards CO<sub>2</sub> was added to the system until reaching a pressure of 40 bar. The reaction proceeded under stirring during 24 h. After completion of the reaction the system was weighted, and a 4.8 wt% of CO<sub>2</sub> uptake was obtained. <sup>1</sup>H-NMR (400 MHz, d<sub>6</sub>-DMSO): δ: 1.59-1.65 (m, 12H), 1.87 (quint, J = 6 Hz, 4 H), 2.14 (dd, J<sub>1</sub> = 14 Hz, J<sub>2</sub> = 6 Hz, 1H), 2.40 (dd, J<sub>1</sub> = 16 Hz, J<sub>2</sub> = 4 Hz, 1H), 2.67-2.69 (m, 4H), 2.83 (bs, 0.2H), 3.23 (t, J = 6 Hz, 4H), 3.32 (m), 3.43 (t, J = 6 Hz, 4 H), 3.48-3.50 (m, 4H) ppm. <sup>13</sup>C-NMR (100 MHz, d<sub>6</sub>-DMSO): δ: 19.27, 23.14, 23.74, 26.26, 28.45, 29.32, 31.56, 36.63, 37.94, 38.51, 47.88, 48.58, 52.69, 53.19, 158.29, 165.12, 174.58, 174.87, 174.93, 174.94 ppm. FTIR (KBr): 3426, 3234, 3106, 3034, 2936, 2863, 2808, 2689, 1648, 1588, 1473, 1445, 1398, 1357, 1324, 1270, 1246, 1207, 1160, 1107, 1091, 1076, 1009, 985, 900, 833, 692, 663, 611, 531 cm<sup>-1</sup>.

### 3 RESULTS AND DISCUSSION

In the present report is tested, in the context of CO<sub>2</sub> capture, the aminoacid aspartic acid (Asp), containing one amine and two carboxylic groups, in combination with two equivalents of an organic superbase, DBU (Figure 3):



**Figure 3:** Individual components, DBU and Aspartic acid. Resulting salt, [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>], and reactional mixture, previous, [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>] + H<sub>2</sub>O, and after reaction with CO<sub>2</sub>, [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>] + H<sub>2</sub>O + CO<sub>2</sub>, the later with composition based on FTIR and NMR analysis.

The salt [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>] is obtained after completion of an atom-economic acid-base reaction, using a sustainable solvent (ethanol). The identity of the salt is confirmed by the modification of the frequency of the C=N stretch in DBU moiety in FTIR spectrum from 1610 to 1649 cm<sup>-1</sup> (Table 1), which, according Galezowski et al [18] is indicative of protonation of the DBU moiety of the salt.

System/FTIR (cm <sup>-1</sup> )	C=N stretch DBU moiety	Carbamate NCO <sub>2</sub> <sup>-</sup>	Bicarbonate CO <sub>3</sub> H <sup>-</sup>	Ammonium -NH <sub>3</sub> <sup>+</sup>	Carboxylic moiety
DBU	1610	-	-	-	-
Aspartic acid	-	-	-	3125 (s, br)	1684 1645 1615 1400
[DBUH <sup>+</sup> ] <sub>2</sub> [Asp <sup>2-</sup> ]	1649	-	2937 (l)	3128 (l)	1587 1397
[DBUH <sup>+</sup> ] <sub>2</sub> [Asp <sup>2-</sup> ] + H <sub>2</sub> O	1648	-	2937 (l)	3122 (m)	1589 1399
[DBUH <sup>+</sup> ] <sub>2</sub> [Asp <sup>2-</sup> ] + H <sub>2</sub> O + CO <sub>2</sub>	1648	1009 832	2936 (s) 835 692	3106 (s)	1588 1398

**Table 1:** FTIR characteristic bands of the relevant functional groups present in reactional mixture, previous and after reaction with CO<sub>2</sub>, salt responsible for its reactivity and correspondent individual components. s – strong band, m – medium, l – low intensity band, br – broad. The systems were evaluated in KBr matrix.

In the same spectrum there's the indication that the carboxylic acid groups are deprotonated, by a strong absorption band at 1587 cm<sup>-1</sup> and a weak band at 1397 cm<sup>-1</sup> [19]. Following the same trend, the <sup>13</sup>C-NMR spectrum is indicative of protonation of DBU moiety in the salt as the (N)(C)C=N peak at 163.96 ppm reveal of a more unshielded chemical environment than in initial DBU (159.54 ppm) – Table 2. When water (0.32 g.) is added to the salt (1 g.) there's no significant modification on the relevant FTIR bands and NMR peaks (Tables 1 and 2). Differently, when CO<sub>2</sub> is added to the mixture [DBUH<sup>+</sup>]<sub>2</sub>[Asp<sup>2-</sup>] + H<sub>2</sub>O, modification in the FTIR profile is evident: The band at 2936 cm<sup>-1</sup> becomes strong, differently from the salt and respective aqueous mixture, both presenting a low intensity band on that region. This evident increment correspond to the existence of bicarbonate in the reactional mixture [20], other relevant bands (835 and 692 cm<sup>-1</sup>) in the mixture, that are inexistent previous to the reaction with CO<sub>2</sub> confirm the identity of bicarbonate. Furthermore, the persistence of the bands at 1648, 1588 and 1398 cm<sup>-1</sup> are indicative of protonation of DBU and deprotonation of the carboxylic functionalities of the aminoacid moiety. Moreover, the FTIR spectrum is indicative of carbamate and ammonium functionalities by the presence of characteristic bands at 1009 and 832 cm<sup>-1</sup> (carbamate) and a strong band centred a 3106 cm<sup>-1</sup> (ammonium) – Table 1. The NMR spectra (Table 2), confirm the analysis of FTIR spectrum: The existence of different peaks in the region of 150-180 ppm in the <sup>13</sup>C-NMR spectrum, the first at 158.29 ppm, possibly corresponding to bicarbonate [21], the significantly displaced peak of (N)(C)C=N of DBU (165.12 ppm), when compared to equivalent peak in the salt and aqueous mixture, indication of increment of the acidity of the media after reaction with CO<sub>2</sub> (Figure 3). The remaining peaks

(173-175 ppm) correspond to one carbamate and slightly different carboxylates of the different aminoacid moieties – Table 2 and Figure 3. The number of intense, three bond-distance spots observed in relevant zone of HMBC spectrum correspond to the exact number of combinations of correlations between protons  $\alpha$  or  $\beta$  and quaternary carbons of carboxylates and carbamate (Table 2). Combination of the  $^1\text{H-NMR}$  and HMBC spectra of the mixture  $[\text{DBUH}^+]_2[\text{Asp}^{2-}] + \text{H}_2\text{O} + \text{CO}_2$  is indicative that 26% of the captured  $\text{CO}_2$  is in the form of carbamate, and the remaining 74% is in the form of bicarbonate, leading to a total of 4.8 wt% of  $\text{CO}_2$  captured by the aqueous solution of the prepared salt. A value comparable with the commercial systems already in the market.

System/NMR (ppm)	(N)(C) $\underline{\text{C}}=\text{N}$ DBU moiety	$\text{NCO}_2^-$ $\text{CO}_2\text{H}^-$ Carboxylic moiety	H( $\alpha$ ) H( $\beta$ ) a.a.	( $^1\text{H},^{13}\text{C}$ ) Intense 3 bond-distance correlations
	$^{13}\text{C-NMR}$	$^{13}\text{C-NMR}$	$^1\text{H-NMR}$	HMBC
DBU	159.54	-	-	-
Aspartic acid	-	179.87 (D <sub>2</sub> O pH 10)[20]	2.66 $\beta_1$ 2.80 $\beta_2$ 3.89 $\alpha$ (D <sub>2</sub> O pH 7)[22]	-
$[\text{DBUH}^+]_2[\text{Asp}^{2-}]$	163.96	174.25 175.05	2.00 $\beta_1$ 2.35 $\beta_2$ 3.30 $\alpha$	-
$[\text{DBUH}^+]_2[\text{Asp}^{2-}] + \text{H}_2\text{O}$	163.89	173.23 176.87	2.04 $\beta_1$ 2.34 $\beta_2$ 3.32 $\alpha$	-
$[\text{DBUH}^+]_2[\text{Asp}^{2-}] + \text{H}_2\text{O} + \text{CO}_2$	165.12	158.29 173.62 174.58 174.87 174.93 174.94	2.14 $\beta_1$ 2.39 $\beta_2$ 3.24 $\alpha$ 3.32 $\alpha'$	(2.12, 174.48) (2.16, 175.14) (2.38, 175.08) (2.42, 175.06) (3.24, 174.69) (3.31, 174.48) (3.34, 174.54)

**Table 2:** Relevant NMR characteristic peaks and correlations of the reactional mixture, previous and after reaction with  $\text{CO}_2$ , salt responsible for its reactivity and correspondent individual components.

## 4 CONCLUSIONS

The method here presented for  $\text{CO}_2$  capture constitutes a straightforward alternative to the commercial systems already in the market, offering simplicity in the preparative steps and low cost of the components of the  $\text{CO}_2$  capture system.

It was obtained a wt% of  $\text{CO}_2$  uptake of 4.8%, a value in the same order of magnitude of the commercial systems already in the market. There's a strong indication that captured carbon dioxide is in the form of bicarbonate (74%) and carbamate (26%).

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