

# The Nature of Carbon Dioxide in Bare Ionic Liquids

Marcileia Zanatta,<sup>[a, b]</sup> Nathália M. Simon,<sup>\*[a]</sup> and Jairton Dupont<sup>\*[a, c]</sup>

Ionic liquids (ILs) are among the most studied and promising materials for selective CO<sub>2</sub> capture and transformation. The high CO<sub>2</sub> sorption capacity associated with the possibility to activate this rather stable molecule through stabilization of ionic/radical species or covalent interactions either with the cation or anion has opened new avenues for CO<sub>2</sub> functionalization. However, recent reports have demonstrated that another simpler and plausible pathway is also involved in the sorption/activation of CO<sub>2</sub> by ILs associated with basic anions. Bare ILs or IL solutions contain almost invariable significant amounts of

water and through interaction with CO<sub>2</sub> generate carbonates/bicarbonates rather than carbamic acids or amidates. In these cases, the IL acts as a base and not a nucleophile and yields buffer-like solutions that can be used to shift the equilibrium toward acid products in different CO<sub>2</sub> reutilization reactions. In this Minireview, the emergence of IL buffer-like solutions as a new reactivity paradigm in CO<sub>2</sub> capture and activation is described and analyzed critically, mainly through the evaluation of NMR data.

## 1. Introduction

■ ■ Please provide institutional and/or personal Twitter handle if available. ■ ■ There is a growing and urgent global need to find commercially viable end-use opportunities for CO<sub>2</sub>.<sup>[1,2]</sup> The ideal process would certainly be a one-pot solution in which the device could capture, activate, and transform the CO<sub>2</sub> available from different sources (ideally from air and exhaust gases).<sup>[3]</sup> Ionic liquids (ILs, Figure 1), mainly those that are thermally, photo-, electro-, and chemically stable and display very low vapor pressures,<sup>[4]</sup> are among the most promising materials to perform this multitask transformation.<sup>[5,6]</sup>

The first report showing that certain ILs can sorb up to 0.6 mole fraction of CO<sub>2</sub> at 8 MPa<sup>[7]</sup> has opened a new window of opportunity for CO<sub>2</sub> capture and transformation. Indeed, CO<sub>2</sub> capture and transformation in ILs through chemical hydrogenation<sup>[8–12]</sup> and electroreduction<sup>[13–15]</sup> to generate chemical commodities has become a blooming and promising field of academic and industrial interest.<sup>[16]</sup> In most cases, the IL is structured as a contact ion pair, even if diluted in high-dielectric-constant solvents, and this supramolecular organization is

mainly responsible for its properties.<sup>[17–19]</sup> In fact, most ILs contain residual water that is extremely difficult to remove because it is trapped inside the 3D supramolecular network of the ILs.<sup>[20]</sup> Bare ILs are those neat ILs that contain invariable “trapped” water, even in hydrophobic ones. In rare cases, pure ILs can be obtained, for example, by distillation.<sup>[21]</sup> A pronounced effect can be observed in ILs with basic anions, as they can absorb even more water from the air than those with nonbasic anions.<sup>[22]</sup> Experimental and theoretical studies demonstrated the formation of a complex between H<sub>2</sub>O and anions connected by a H-bond with 8–16 kJ mol<sup>-1</sup> binding energy, generating a 3D H-bond network structure.<sup>[20,22–24]</sup> The determination of the exact water content in ILs is extremely difficult to determine, and is usually estimated by Karl–Fischer titration and cyclic voltammetry.<sup>[25]</sup> It is clear that bare ILs contains at least one molecule of water per ion pair, and most usually possess seven water molecules per ion pair.<sup>[26]</sup> Hence, in most cases, we are dealing with IL aqueous solutions.<sup>[18]</sup>

This aqueous issue is more evident in cases involving CO<sub>2</sub> capture from flow gases that invariably contain water (5–7% by volume). Nonetheless, even though water does not significantly affect the supramolecular organization (Figure 2), it is important to keep in mind that the amount of residual or added water in the ILs is a determining factor in its sorption

[a] Dr. M. Zanatta, Prof. Dr. N. M. Simon, Prof. Dr. J. Dupont  
Institute of Chemistry—Universidade Federal do Rio Grande do Sul  
Av. Bento Gonçalves, 9500 Porto Alegre 91501-970 RS (Brazil)  
E-mail: nathalia.marcolin@ufrgs.br  
jairton.dupont@ufrgs.br

[b] Dr. M. Zanatta  
i3N|Cenimat, Materials Science Department  
School of Science and Technology (FCT)  
NOVA University of Lisbon  
Caparica, 2829-516, (Portugal)

[c] Prof. Dr. J. Dupont  
Visiting Professor—SENECA ■ ■ Please check, relation to authors unclear. ■ ■  
Facultad de Química  
Universidad De Murcia  
30.100. Murcia (Spain)

■ The ORCID identification number(s) for the author(s) of this article can be found under:  
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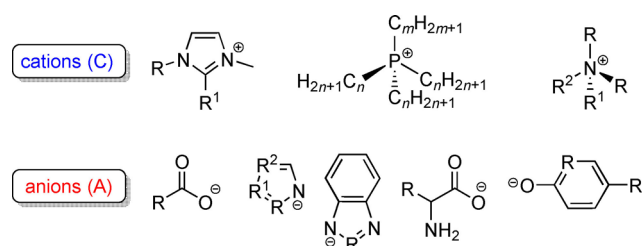


Figure 1. Examples of ILs containing different cations and basic anions.

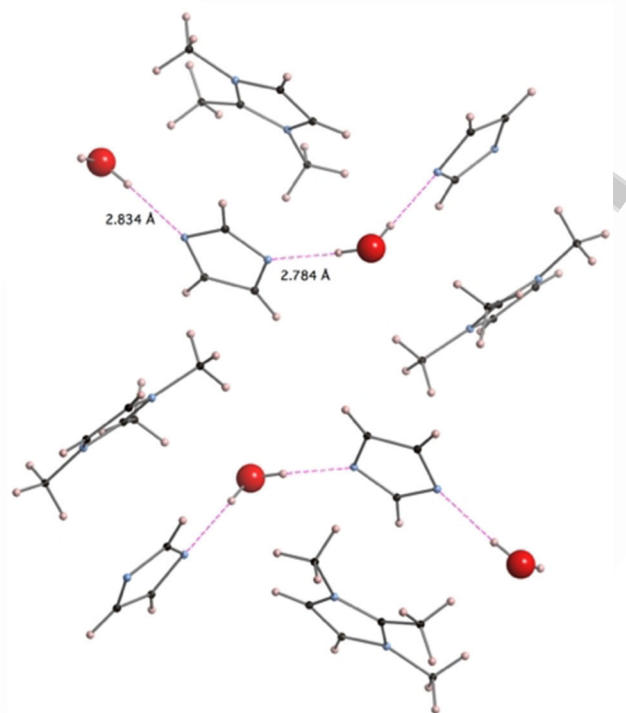
Marcileia Zanatta received her PhD (2017) in Chemistry at the Universidade Federal do Rio Grande do Sul (UFRGS), Brazil. She received an award for her PhD project presentation from the Nuclear Magnetic Resonance Users Association (AUREMN 2016) and the recognition of the journal Magnetic Resonance in Chemistry (MRC). Dr. Zanatta worked in Dupont's group between 2012 and 2019 and as an Assistant Professor at UFRGS (2018) in the Inorganic Department. Currently, she is an Associate Researcher at NOVA University of Lisbon (UNL). Her domain of specialization is Chemistry and Materials with a special focus on catalysis, CO<sub>2</sub> capture and valorization, ILs, and NMR spectroscopy. Her present research interests include sustainable processes and green chemistry.



Nathália M. Simon obtained her PhD in Chemistry in 2017 from Universidade Federal do Rio Grande do Sul (UFRGS). She worked in Dupont's group between 2011 and 2019. Recently she became a Professor in the Department of Physical Chemistry at the Institute of Chemistry at UFRGS. Since her MSc, her research interests have included ILs and poly(ILs), with emphasis on their application for CO<sub>2</sub> sorption and nanometallic catalysis. Besides these topics, she has recently added chemistry education as a research interest.



Jairton Dupont has been a Professor in the Department of Organic Chemistry at UFRGS since 1992. He gained his PhD in Chemistry from Louis Pasteur University of Strasbourg, France, and undertook postdoctoral work at the Dyson Perrins Laboratory, University of Oxford, UK. Between 2014 and 2017, he served as a Professor of Sustainable Chemistry (EPSRC/ GSK Professor of Sustainable Chemistry) at the University of Nottingham, UK. He has received more than 20 Awards and Honours, such as a Royal Society Fellowship, SBM Simão Mathias Medal (Brazil, 2005), Humboldt Young Research Award (Germany), Elsevier-CAPES Scopus Award, TWAS Chemistry Award (2011), and the title of doctor honoris causa at the University of Murcia, Spain (2017). He is currently an associate editor of the *New Journal of Chemistry* (RSC), a fellow of the Brazilian Academy of Sciences, and head of the Chemistry Institute (UFRGS).



**Figure 2.** X-ray structure of H<sub>2</sub>O@[MMMI][Im] (MMMI = ■■■ please define. ■■■ Im = 1,2,3-trimethylimidazolium imidazolate), adapted from Zanatta et al.<sup>[20]</sup>

capacity. This is probably the main factor causing different interpretations regarding the effect of humidity on CO<sub>2</sub> capture results.

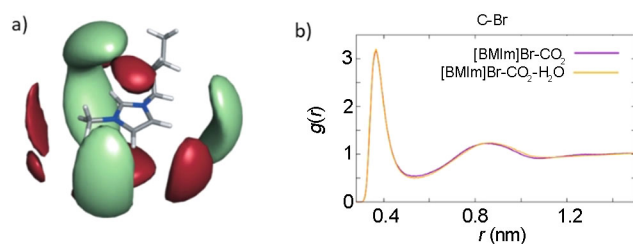
It is important to note that, in most cases, the total CO<sub>2</sub> sorption is reported, and therefore, it corresponds to the bare IL, that is, it contains the contribution of both water and the IL. Note that CO<sub>2</sub> solubility is relatively high in water (Henry coefficient =  $3.3 \times 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1}$ )<sup>[20]</sup> and should be not neglected. Therefore, in most cases, the reported CO<sub>2</sub> sorption data are for IL aqueous solutions and not for the "pure" fluid. Moreover, in various cases, the interaction of the IL pair changes the reactivity of the trapped water, which can easily react with substrates, products, and even with the IL.<sup>[8,9,19,27–30]</sup>

In this contribution, the different modes of interaction of CO<sub>2</sub> with bare ILs containing both nonbasic and mainly basic anions will be presented and discussed critically, considering recent examples reported in the literature. Finally, it will be demonstrated that simple concepts of acid–base chemistry can be used to explain and to design new ionic fluids for CO<sub>2</sub> capture and activation.

## 2. CO<sub>2</sub> in Nonbasic ILs

The interaction of CO<sub>2</sub> with ILs containing nonbasic anions is well established (experimentally and theoretically)<sup>[31]</sup> and occurs with little or no disruption of the supramolecular organization of the ILs. The CO<sub>2</sub> is located near the nonpolar cavities of the ion pair, and does compete with the same sites as the residual water (invariably present in almost all ILs),<sup>[20]</sup> which re-

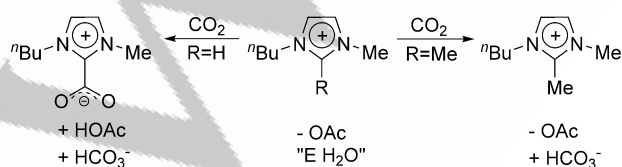
sides close to the more ionic nanoregions of the ion pairs.<sup>[32]</sup> Carbon dioxide is solvated preferentially in the vicinity of the anion and in the nonpolar region of imidazolium ILs (Figure 3a).<sup>[33]</sup> The addition of water into the system does not disrupt the coordination patterns, which remain almost unaltered (Figure 3b).<sup>[34]</sup> The nonbasic ILs present low sorption capacity under atmospheric pressure ( $> 0.2 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{IL}}$  should this actually be  $< 0.2$ ? this type of IL will not be the main focus of this Minireview.)<sup>[37]</sup> By contrast, various ILs containing basic anions display multimolar  $\text{CO}_2$  sorption (Table 1).



**Figure 3.** Molecular dynamics simulations (MDS) involving ILs and  $\text{CO}_2$ . a) Spatial distribution functions (SDFs) for the  $\text{PF}_6^-$  anion (green) and  $\text{CO}_2$  (red) near the imidazolium cation for the interaction of  $\text{CO}_2$  with 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF<sub>6</sub>) IL (adapted from Corvo et al.<sup>[32]</sup>) b) Radial distribution functions (RDFs) corresponding to systems containing IL ([BMIm]Br),  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . C( $\text{CO}_2$ )-Br(anion) (adapted from Simon et al.<sup>[34]</sup>).

### 3. $\text{CO}_2$ in Basic ILs

In the case of ILs containing basic anions such as acetate, imidazolate, and triazolates, the situation is far from clear. It is usually assumed that there is a covalent interaction of  $\text{CO}_2$  either with the cation or the anion, hence absorbing and activating  $\text{CO}_2$  at atmospheric pressure (Scheme 1). There are dozens of reports indicating that the appropriate geometrical and electronic changes in both cation and anion can furnish materials capable of absorbing multimolar quantities of  $\text{CO}_2$ , and reduce the overpotential for  $\text{CO}_2$  reduction.<sup>[38]</sup> The activation of  $\text{CO}_2$  in these cases is probably caused by the breaking of the  $\text{CO}_2$  linearity geometry, and in electroreductions, it is also assumed to be attributable to the stabilization of the  $\text{CO}_2$  radical anion ( $\text{CO}_2^{\cdot-}$ ) provided by the cation (usually imidazolium).<sup>[15,29,39]</sup> In some cases, the formation of bicarbonate/carbonate has been claimed as a result of the interaction of wet ILs containing phosphonium and ammonium cations associated with basic anions such as carboxylates or amino acids.<sup>[40,41]</sup>



**Scheme 1.** Products from the interaction of "wet" [BMIm][OAc] and [BMMIm][OAc] with  $\text{CO}_2$ .

However, in most of these cases, it is claimed that basic (and even super-basic) anions perform a nucleophilic attack on  $\text{CO}_2$ . These claims are based mainly on the single evidence provided by the presence of a signal at around 158–164 ppm in the  $^{13}\text{C}$  NMR spectra of the reaction mixture after  $\text{CO}_2$  sorption, regardless of whether the nature of the claimed product is carbamic acid or amidate. Note that the pH of most of these ILs containing basic anions can be as high as 14, as in the case of imidazolate anions, forming alkali-like solutions. The exact nature of the structure of the material(s) formed by the interaction of  $\text{CO}_2$  with ILs containing basic anions is of paramount importance for the design of more effective materials for  $\text{CO}_2$  capture, activation, and transformation. Analysis of the published data on the interaction of  $\text{CO}_2$  with ILs containing basic anions clearly indicates that the salt is indeed a base and not a nucleophile, and the primary and major product formed by interaction with  $\text{CO}_2$  is carbonate/bicarbonate and not  $\text{CO}_2$  covalently attached to the anion.

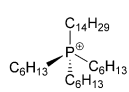
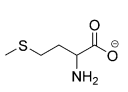
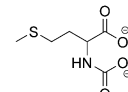
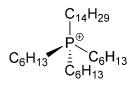
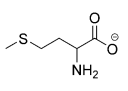
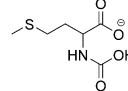
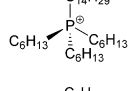
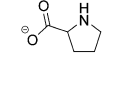
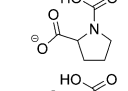
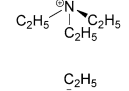
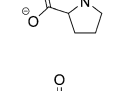
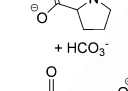
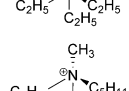
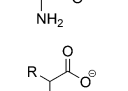
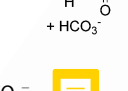
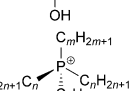
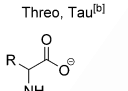

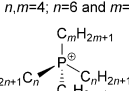
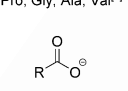
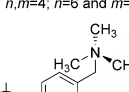
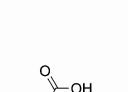
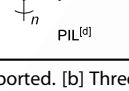
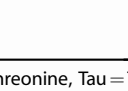
Table 1 shows the claimed structures of the products resulting from the interaction of  $\text{CO}_2$  and ILs containing basic anions and the respective  $^{13}\text{C}$  chemical shifts attributed to the carbonyl groups. The reported chemical shifts of the carboxylic species are around 160 ppm, similar to the range expected for carbonate/bicarbonate, as determined by both theoretical and experimental studies.<sup>[42]</sup> Only in the case of [BMIm][OAc] was the structure of the carboxylic-imidazolium product firmly established by a series of techniques (including X-Ray structure).<sup>[43]</sup> In many cases, only weak evidence was provided for the formation of  $\text{CO}_2$ -anion adducts. The first important point is that most of these ILs contain water (confined) and the water molecules are activated in the confined ionic spaces (Figure 3), and the presence of a base can shift the equilibrium towards hydronium-hydroxide ions. The possibility of reaction between  $\text{CO}_2$  and this pocket water must never be disregarded. Therefore, it is clear that  $\text{CO}_2$  in basic media will produce carbonate and/or bicarbonate, even in the case of an IL containing the acetate anion (1-butyl-2,3-dimethylimidazolium acetate [BMMIm][OAc]) in which the C-2 imidazolium position is blocked (Scheme 1).<sup>[44]</sup>

Controversial results are often found in the literature regarding mixtures between [BMIm][OAc],  $\text{CO}_2$ , and water.<sup>[62–65]</sup> Combining NMR analysis and molecular dynamics simulations (MDS), Gomes and co-workers observed the formation of a cation- $\text{CO}_2$  complex resulting from the abstraction of H-2 of the imidazolium cation in mixtures between [BMIm][OAc] and  $\text{CO}_2$ .<sup>[33]</sup> Additionally, a signal around 160 ppm was detected in the  $^{13}\text{C}$  spectrum, probably related to bicarbonate species formed from residual water present on the IL. The addition of water in the system decreased the sorption capacity, as no new signals were detected in the NMR spectrum. These results suggest that there could be an ideal ratio between IL and water, in which the  $\text{H}_2\text{O}$  molecules are activated by the anion. The increases in water amount could result in ion-pair separation by solvation and water deactivation. Allied to the residual water present in the ILs, the flue gas contains a considerable amount of water (e.g., 5–7% by volume), and understanding

**Table 1.** Selected examples of the products with the corresponding attributed chemical shifts for COO moieties resulting from the interaction of CO<sub>2</sub> with ILs containing basic anions.

| Entry | Cation | Anion | CO <sub>2</sub> product<br>(attributed by the authors) | COO- shift [ppm]  | Sorption total<br>[mol <sub>CO<sub>2</sub></sub> /mol <sub>IL</sub> ] | Conditions<br>T [°C]/P [bar]                                      | Ref. |
|-------|--------|-------|--|---|---|---|------|
| 1     |        |       |  | 160.0   | 0.95  | 40/10   | [45] |
| 2     |        |       |  | 161.3   | 1.60  | 25/1<br>(60 cm <sup>3</sup> min <sup>-1</sup> )                   | [46] |
| 3     |        |       |  | ca. 160 (HCO <sub>3</sub> <sup>-</sup> )<br>ca. 145 (N-CO <sub>2</sub> )                | 0.55 (HCO <sub>3</sub> <sup>-</sup> )<br>0.35 (N-CO <sub>2</sub> )    | 25/1  | [47] |
| 4     |        |       |  | – <sup>[a]</sup>  | 1.03  | 23/1  | [48] |
| 5     |        |       |  | 160.3   | 0.65  | 22/50 cm <sup>3</sup> min <sup>-1</sup><br>■■ please check.<br>■■ | [49] |
| 6     |        |       |  | 160.2   | 0.82  | 22/1<br>(50 cm <sup>3</sup> min <sup>-1</sup> )                   | [49] |
| 7     |        |       |  | 163.9   | 1.57  | 20/1  | [50] |
| 8     |        |       |  | 162.9   | 0.79  | 22/1<br>(50 cm <sup>3</sup> min <sup>-1</sup> )                   | [51] |
| 9     |        |       |  | 164.2   | 0.53  | 55/1  | [52] |
| 10    |        |       |  | ca. 160 (HCO <sub>3</sub> <sup>-</sup> )<br>ca. 150 (N-CO <sub>2</sub> )                | 0.77 (HCO <sub>3</sub> <sup>-</sup> )<br>0.18 (N-CO <sub>2</sub> )    | 25/1  | [47] |
| 11    |        |       |  | 160.2   | 1.20  | 22/1<br>(50 cm <sup>3</sup> min <sup>-1</sup> )                   | [49] |
| 12    |        |       |  | 160.3   | 0.23  | 22/1<br>(50 cm <sup>3</sup> min <sup>-1</sup> )                   | [49] |
| 13    |        |       |  | 158.8   | 0.82  | 30/1<br>(60 cm <sup>3</sup> min <sup>-1</sup> )                   | [53] |
| 14    |        |       |  | 166.6 (N-CO <sub>2</sub> )<br>159.3 (O-CO <sub>2</sub> )                                | 1.58  | 20/1  | [54] |
| 15    |        |       |  | 160.0   | 0.26  | –/1   | [55] |
| 16    |        |       |  | 177.6 (N-CO <sub>2</sub> )<br>159.9 (O-CO <sub>2</sub> )                                | 1.40  | 30/1  | [56] |
| 17    |        |       |  | ■■ Please check product. ■■ 156.8<br>(O-CO <sub>2</sub> )<br>163.5 (N-CO <sub>2</sub> ) | 1.69  | 40/1  | [57] |

**Table 1.** (Continued)

| Entry | Cation  | Anion   | CO <sub>2</sub> product (attributed by the authors)  | COO <sup>-</sup> shift [ppm]                            | Sorption total [mol <sub>CO<sub>2</sub></sub> /mol <sub>IL</sub> ] | Conditions T [°C]/P [bar]                         | Ref. |
|-------|---|---|--|---|--|---|------|
| 18    |    |    |                                     | 160.0   | 0.93 (0.74 chemical/<br>0.19 physical)                             | 25/1  | [58] |
| 19    |    |    |                                     | 176.0   | ca. 1.0 <sup>[e]</sup>   | 25/1  | [59] |
| 20    |    |    |                                     | 158.4   | ca. 1.0 <sup>[e]</sup>   | 25/1  | [59] |
| 21    |    |    | <br>+ HCO <sub>3</sub> <sup>-</sup> | 162.6 (N-CO <sub>2</sub> )<br>159.4 (HCO <sub>3</sub> ) | ca. 1.0 <sup>[e]</sup>   | 25/1<br>(flow)                                    | [40] |
| 22    |    |    | <br>+ HCO <sub>3</sub> <sup>-</sup> | 163.3 (N-CO <sub>2</sub> )<br>159.4 (HCO <sub>3</sub> ) | ca. 1.0 <sup>[e]</sup>   | 25/1<br>(flow)                                    | [40] |
| 23    |    |    | HCO <sub>3</sub> <sup>-</sup><br>   | 164.4 (N-CO <sub>2</sub> )<br>160.6 (HCO <sub>3</sub> ) | – <sup>[a]</sup>   | 25/1<br>(2.36 cm <sup>3</sup> min <sup>-1</sup> ) | [60] |
| 24    |   |   | HCO <sub>3</sub> <sup>-</sup>  | 161.5   | 1.01–1.10  | 25/5  | [41] |
| 25    |  |  | HCO <sub>3</sub> <sup>-</sup>  | 161.5   | 0.33–0.50  | 25/5  | [41] |
| 26    |  |  | HCO <sub>3</sub> <sup>-</sup>  | 161.0   | – <sup>[a]</sup>   | 25/1<br>(flow)                                    | [61] |

[a] Not reported. [b] Threo = Threonine, Tau = Taurine. [c] Gly = Glycine; Pro = Proline; Ala = Alanine; Val = Valine. [d] Poly(IL). [e] Near to stoichiometric.

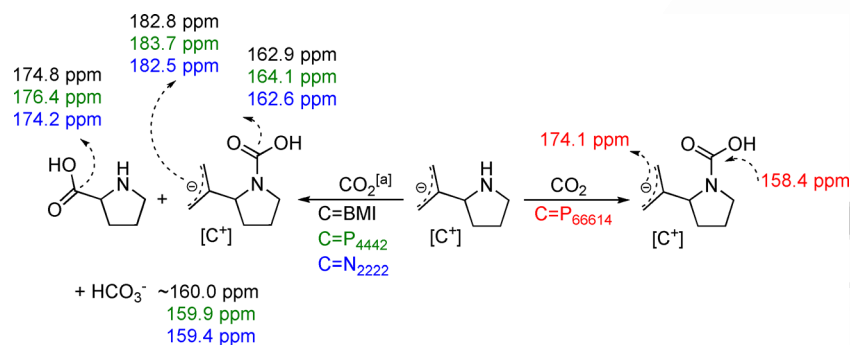
the effect and the nature of water is critical for post-combustion CO<sub>2</sub> capture and utilization.<sup>[47]</sup>

Conflicting structural attribution of the products resulting from the interaction between CO<sub>2</sub> and ILs is also evident in the case of proline-containing ILs (Scheme 2). Upon association with a tetraalkylphosphonium cation ([P<sub>66614</sub>])<sup>+</sup> a product resulting from the nucleophilic attack of the amine by CO<sub>2</sub> was proposed on the basis of IR studies, but the reported <sup>13</sup>C NMR indicated quite a higher-field <sup>13</sup>C chemical shift (158.4 ppm) than would be expected for such a structure,<sup>[59]</sup> which is in the expected range for a bicarbonate.<sup>[40]</sup> In the case of the proline associated with the imidazolium cation and the atmospheric pressure sorption of CO<sub>2</sub>, three main products were observed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy: bicarbonate, proline, and CO<sub>2</sub>-proline adduct (Scheme 2).<sup>[34]</sup>

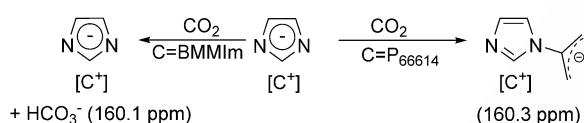
A similar idea can be extended to other amino-acid-based ILs. Recently, CO<sub>2</sub> absorption in anion aqueous solutions (50 wt%) of tetraalkylammonium-based ILs with threonine

(Threo) and taurine (Tau) was studied by liquid- and solid-state <sup>13</sup>C NMR and <sup>15</sup>N magic-angle spinning NMR spectroscopy.<sup>[60]</sup> A precipitated product formed by the reaction with CO<sub>2</sub> was analyzed by solid-state NMR spectroscopy, demonstrating the formation of neutral threonine (or taurine) in zwitterionic form. Therefore, they assigned the resonance line at 164.4 ppm to the formation of the carbamate anion and the resonance line at 160.6 ppm to carbamic acid.<sup>[66]</sup>

Further contradictions were reported in the case of the imidazolate anion associated with phosphonium and imidazolium cations (Scheme 3). If associated with the phosphonium cation, a CO<sub>2</sub>-imidazolate adduct was claimed upon interaction with CO<sub>2</sub>, again on the basis of <sup>13</sup>C NMR data and on the signal intensity corresponding to the carbonyl group increases upon addition of water;<sup>[49]</sup> in this case, again, the <sup>13</sup>C chemical shift observed at 160.3 ppm is in the bicarbonate range. However, if the imidazolate anion is associated with the imidazolium cation, the interaction with CO<sub>2</sub> generates bicarbonate and not



**Scheme 2.** Reported structures of the products resulting from the interaction of CO<sub>2</sub> with prolinatate associated with imidazolium and phosphonium cations (adapted from Simon et al.<sup>[34]</sup>).

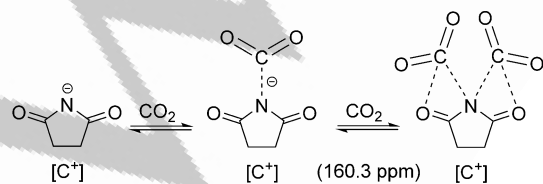


**Scheme 3.** Proposed structures for the interaction of CO<sub>2</sub> with ILs associated with the imidazoliate anion. [a] Depending on experimental parameters: CO<sub>2</sub> pressure, quantity of water, and pH of solution.

any anion–CO<sub>2</sub> adduct, as demonstrated by a series of homo- and heteronuclear NMR experiments.<sup>[44]</sup>

More intriguing results were reported on the use of imide-based ILs that display an impressive gravimetric CO<sub>2</sub> capacity (up to 22 wt%), namely tri-*n*-butyl-ethyl-phosphonium (P<sub>4442</sub>)-based ILs associated with diacetamide (DAA) and succinimide (Suc) anions.<sup>[67]</sup> Through a combination of quantum chemical calculations, FTIR spectroscopy, and <sup>13</sup>C NMR investigations involving the cooperative interactions between CO<sub>2</sub> and multiple active sites of the preorganized anion, a mechanism has been proposed (Scheme 4). The authors also reported CO<sub>2</sub> capture upon using a similar IL with the addition of an electron-donating group into the anion, again suggesting the idea of cooperative interactions between anion and CO<sub>2</sub>. In the <sup>13</sup>C NMR spectra, a new signal was observed around 159 ppm, attributed to the N–CO<sub>2</sub> interaction, and a shift in the C=O signal of the anions from 195.6 to 188.0–182.8 ppm.<sup>[68]</sup> However, another detailed NMR, IR, and electron-spray-ionization–MS study using similar conditions indicated that the interaction of these amide-based ILs forms bicarbonate instead of the interaction between anion and CO<sub>2</sub>.<sup>[69]</sup>

Recently, in the same context, a strategy to improve CO<sub>2</sub> capture by reducing cation–anion interactions in 2-hydroxyl

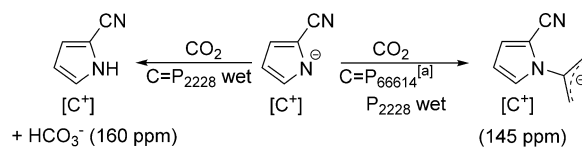


**Scheme 4.** Proposed structures for the interaction of CO<sub>2</sub> with IL containing succinimide anion (adapted from Huang et al.<sup>[67]</sup>).

pyridium (2-Op) anion-based ILs was reported. The <sup>13</sup>C NMR spectrum of [P<sub>4442</sub>][2-Op] after the sorption of CO<sub>2</sub> showed two new signals at 177.6 and 159.9 ppm. The authors attributed the signals to the N and O sites of the [2-Op] anion, cooperatively bound to a CO<sub>2</sub> molecule, respectively.<sup>[56]</sup>

The products obtained using ILs with pyrrolide-based anions for CO<sub>2</sub> sorption were also investigated. Initially, the most accepted pathway suggested the formation of carbamate species. This product was suggested by theoretical calculations, IR spectroscopy, and <sup>1</sup>H NMR data; however, no reports of the <sup>13</sup>C NMR chemical shift have been found.<sup>[70,71]</sup> Recently, Brennecke and co-workers proposed two different mechanisms of sorption for this type of IL: one is more common in dry ILs, and the other more common in wet ILs. The group demonstrated that both pathways do not require the presence of water and may or may not require the presence of CO<sub>2</sub> (Scheme 5). They suggest that in mixtures of ILs + CO<sub>2</sub> + H<sub>2</sub>O, the anion is reprotonated, thus leaving CO<sub>2</sub> to react with the hydroxide to form bicarbonate, as proved by the appearance of a signal around 160 ppm. In addition, the formation of carbamate resulting from the reaction between CO<sub>2</sub> and N of the anion (2-cyanopyrrolide) was also confirmed by the appearance of a new signal around 145 ppm.<sup>[47]</sup>

It is quite intriguing that most reports related to the sorption of CO<sub>2</sub> with ILs associated with basic anions assumed the covalent interaction of CO<sub>2</sub>, whereas the provided evidence also pointed to a simpler and more likely explanation, that is, the formation of bicarbonate/carbonates in a basic solution. It is also evident that the vast majority of bare ILs always contain water and we are dealing, in most cases, with water solutions of ILs or at least with ILs containing confined water.<sup>[18]</sup> The acidity/basicity of these ILs is, therefore, quite dependent upon the amount of water, and the determination of the pH of IL

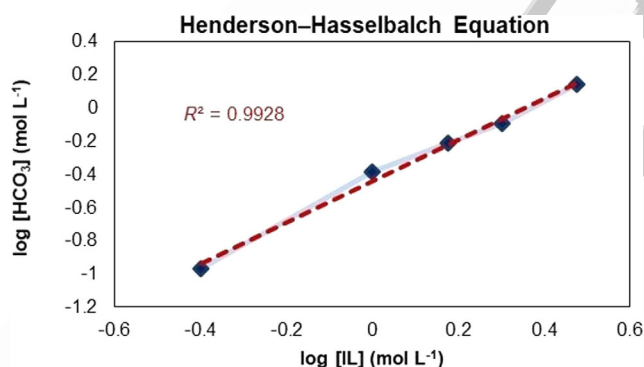


**Scheme 5.** Proposed structures for the interaction of CO<sub>2</sub> with ILs associated with the 2-cyanopyrrolide anion. [a] Chemical shift not reported.

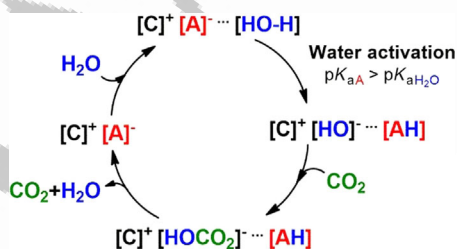
solutions in organic solvents such as MeCN and DMSO is highly important in the presence of “dissolved” CO<sub>2</sub>, in particular for electrochemical reductions<sup>[38]</sup> and chemical reductions.<sup>[13]</sup> For example, the buffering properties of [BMMIm][OAc] have been used to promote the selective hydrogenation of CO<sub>2</sub> to free formic acid.<sup>[8,9]</sup> Moreover, IL/DMSO/H<sub>2</sub>O solution behaves as a buffer-like solution favoring the formation of bicarbonate, which, in turn, provides a constant supply of dissolved CO<sub>2</sub> necessary for the electrochemical reduction to occur efficiently, facilitating the diffusion of CO<sub>2</sub> to the surface of the electrode.<sup>[72]</sup> Furthermore, there are clear effects of bicarbonate buffer concentration on the partial currents of the major products formed by reduction of CO<sub>2</sub> over Cu electrodes. The composition and concentration of electrolyte anions have relatively little effect on the formation of CO, HCOO, C<sub>2</sub>H<sub>4</sub>, and CH<sub>3</sub>CH<sub>2</sub>OH, but have a significant effect on the formation of H<sub>2</sub> and CH<sub>4</sub>.<sup>[73]</sup>

The interaction of CO<sub>2</sub> with bare ILs associated with basic anions (usually contaminated with water) produces carbonate/bicarbonate and the IL solution forms a buffer-like solution. Indeed, the system obtained follows the Henderson–Hasselbalch equation, which is typically employed to describe buffering systems (Figure 4).

The most plausible sorption mechanism for bicarbonate formation in bare ILs is represented in Scheme 6. Basic anions, with higher pK<sub>a</sub> than H<sub>2</sub>O, can activate the water by abstraction of a hydrogen atom to yield hydroxide and a protonated anion, followed by reaction with CO<sub>2</sub> to form bicarbonate/carbonate.



**Figure 4.** Example of the typical buffer-like properties of ILs upon interaction with CO<sub>2</sub> (double log of [BMMIm][Im] solutions in DMSO/H<sub>2</sub>O, 95:5). Adapted from Gonçalves et al.<sup>[29]</sup>



**Scheme 6.** Pathway of bicarbonate formation in bare ILs with basic anions.

Concern about the acceptance of the hygroscopic nature of ILs and the correct determination of signals in NMR analysis has resulted in other recent reports.<sup>[74,75]</sup> Despite the drying procedures adopted, the IL water content is always significant and able to create a ternary system (CO<sub>2</sub> + IL + water). According to Lei and co-workers, the water effect on the gas solubility in ILs can be divided into three distinct scenarios related to cation/anion structure and water amount: 1) degradation (water reacts with the IL); 2) dilution (water dilutes the ILs and inhibits the CO<sub>2</sub> dissolution); and 3) enhancement (the presence of water promotes the CO<sub>2</sub> chemical sorption).<sup>[76]</sup> The reaction pathways of the interaction of CO<sub>2</sub> with ILs containing basic anions probably involves the rapid physical sorption of CO<sub>2</sub>, which is almost instantaneously transformed into bicarbonate/carbonate, and this new basic IL solution promotes the reaction of cations and/or anions with CO<sub>2</sub>, forming new IL adducts. In particular, 1,3-dialkylimidazolium can generate carbenes and the carboxylate adduct, which can act as a CO<sub>2</sub> transferring agent to other substrates present in the medium.<sup>[77]</sup>

The <sup>13</sup>C NMR chemical shift of the CO<sub>2</sub> adducts with imidazolium cations generally appears at approximately 155 ppm.<sup>[34]</sup> The reaction between CO<sub>2</sub> with nitrogenated anions forming carbamate/carbamic acid may appear in a larger range of chemical shifts, from 145 ppm (Table 1, entry 3) to 177 ppm (Table 1, entry 16). The chemical shift for HCO<sub>3</sub><sup>-</sup> is generally reported between 159–161 ppm in <sup>13</sup>C NMR spectra. Moreover, it may appear at higher chemical shift (163–167 ppm) in systems with higher pH (equilibrium toward CO<sub>3</sub><sup>2-</sup>).<sup>[78]</sup> Finally, to assign the structure of the CO<sub>2</sub>–IL adducts unambiguously, it is important to perform multinuclear NMR experiments, with the use of <sup>13</sup>C-enriched compounds (at least <sup>13</sup>C-enriched CO<sub>2</sub>, in FTIR and mass spectrometry). The formation of bicarbonate can be confirmed easily by using <sup>13</sup>CO<sub>2</sub> and D<sub>2</sub>O and performing <sup>13</sup>C and 2D multinuclear NMR experiments such as HMBC, HSQC, and HOESY experiments.<sup>[32,34,40,44,47,64,79,80]</sup>

## 4. Conclusions

Ionic liquids (ILs) containing basic anions such as carboxylates, *N*-heterocycles, and amino acids have been used extensively for CO<sub>2</sub> capture. <sup>13</sup>C NMR and IR spectroscopy are the most common techniques applied to study the ILs–CO<sub>2</sub> sorption mechanisms. The <sup>13</sup>C chemical shifts of the CO<sub>2</sub> adducts are usually the main evidence provided, generating different interpretations for species formed with similar ILs and experimental conditions.

The possible presence of residual water in “neat ILs” and in CO<sub>2</sub> gas should not be ignored as it directly affects the gas solubility and CO<sub>2</sub> sorption mechanism. In addition, it seems that every IL presents an ideal molar fraction of water and IL that leads to activation of the system and increases the sorption. Therefore, if working with bare ILs (invariably containing water) associated with CO<sub>2</sub>, the formation of bicarbonate/carbonates should be considered as possible activation/reaction pathways. Such species can be used as CO<sub>2</sub>-active intermedi-

ates, facilitating reutilization by hydrogenation or photochemical or electrochemical catalysis.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** bicarbonate · buffer solutions · CO<sub>2</sub> capture · ionic liquids · water activation

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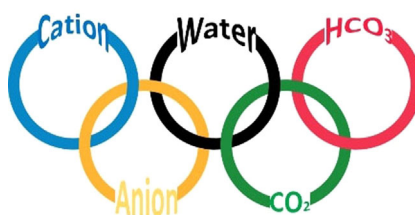
## MINIREVIEWS

M. Zanatta, N. M. Simon,\* J. Dupont\*

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## The Nature of Carbon Dioxide in Bare Ionic Liquids

## Acid-base Games



**Acid-base games:** This Minireview analyzes the role of ionic liquids in the capture and transformation of CO<sub>2</sub>. Bare ionic liquids ILs invariably contain water, and through interaction with CO<sub>2</sub> generate carbonates/bicarbonates rather than carbamic acids or amidates. Here, the IL acts as a base (not a nucleophile). ■  
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Dr. Marcileia Zanatta <http://orcid.org/0000-0002-3080-3627>Prof. Dr. Nathália M. Simon <http://orcid.org/0000-0002-6034-7757>Prof. Dr. Jairton Dupont <http://orcid.org/0000-0003-3237-0770>