The Nature of Carbon Dioxide in Bare Ionic Liquids

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Ionic liquids (ILs) are among the most studied and promising materials for selective CO_2 capture and transformation. The high CO_2 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_2 functionalization. However, recent reports have demonstrated that another simpler and plausible pathway is also involved in the sorption/activation of CO_2 by ILs associated with basic anions. Bare ILs or IL solutions contain almost invariable significant amounts of water and through interaction with CO_2 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_2 reutilization reactions. In this Minireview, the emergence of IL buffer-like solutions as a new reactivity paradigm in CO_2 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_2.[1,2] The ideal process would certainly be a one-pot solution in which the device could capture, activate, and transform the CO_2 available from different sources (ideally from air and exhaust gases).[3] Ionic liquids (ILs, Figure 1), mainly those that are thermally, photo-, electro-, and chemically stable and display very low vapor pressures,[4] are among the most promising materials to perform this multitask transformation.[5, 6]

The first report showing that certain ILs can sorb up to 0.6 mole fraction of CO_2 at 8 MPa[7] has opened a new window of opportunity for CO_2 capture and transformation. Indeed, CO_2 capture and transformation in ILs through chemical hydrogenation[8–12] and electroreduction[13–15] to generate chemical commodities has become a blooming and promising field of academic and industrial interest.[16] 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.[17–19] 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.[20] 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.[21] 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.[22] Experimental and theoretical studies demonstrated the formation of a complex between H_2O and anions connected by a H-bond with 8–16 kJ mol^{-1} binding energy, generating a 3D H-bond network structure.[20, 22–24] 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.[25] 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.[26] Hence, in most cases, we are dealing with IL aqueous solutions.[18]

This aqueous issue is more evident in cases involving CO_2 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

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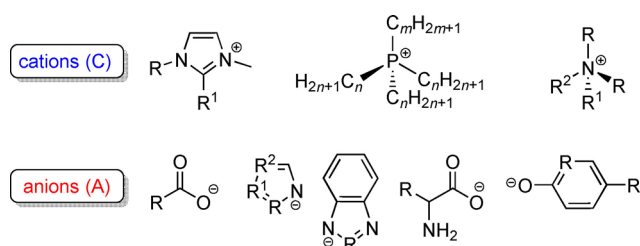The ORCID identification number(s) for the author(s) of this article can be found under:
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Figure 1. Examples of ILs containing different cations and basic anions.

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Jaïrton 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).
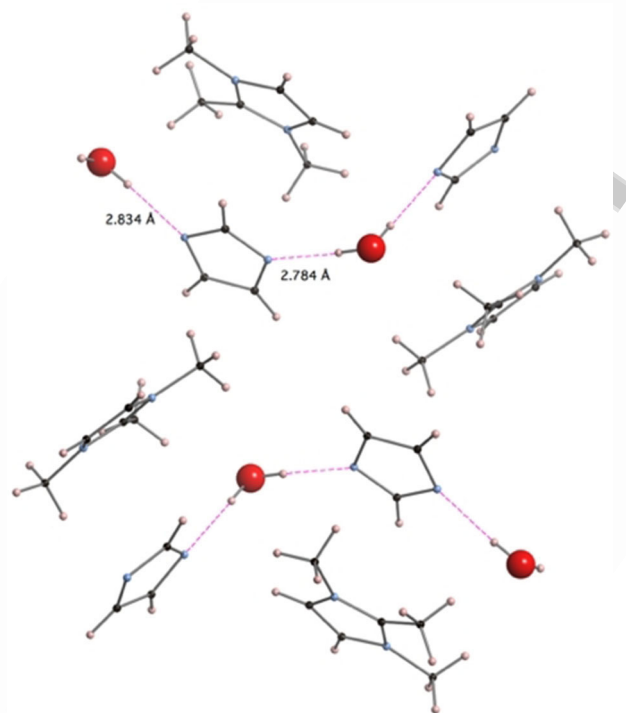
Figure 2. X-ray structure of $H_2O@[MMMIm][Im[$ (MMIm = ■■please define. ■■Im = 1,2,3-trimethylimidazolium imidazolate), adapted from Zanatta et al.[20]

capacity. This is probably the main factor causing different interpretations regarding the effect of humidity on CO_2 capture results.

It is important to note that, in most cases, the total CO_2 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_2 solubility is relatively high in water (Henry coefficient = 3.3×10^{-4} mol m^{-3} Pa^{-1})[20] and should be not neglected. Therefore, in most cases, the reported CO_2 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.[8,9,19,27–30]

In this contribution, the different modes of interaction of CO_2 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_2 capture and activation.

2. CO_2 in Nonbasic ILs

The interaction of CO_2 with ILs containing nonbasic anions is well established (experimentally and theoretically)[31] and occurs with little or no disruption of the supramolecular organization of the ILs. The CO_2 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),[20] which re-

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sides close to the more ionic nanoregions of the ion pairs.[32] Carbon dioxide is solvated preferentially in the vicinity of the anion and in the nonpolar region of imidazolium ILs (Figure 3 a).[33] The addition of water into the system does not disrupt the coordination patterns, which remain almost unaltered (Figure 3 b).[34] The nonbasic ILs present low sorption capacity under atmospheric pressure (>0.2 mol_{CO_2}/mol_{IL} ■■should this actually be <0.2?■■ 🗨 this type of IL will not be the main focus of this Minireview. [36,37] By contrast, various ILs containing basic anions display multimolar CO_2 sorption (Table 1).
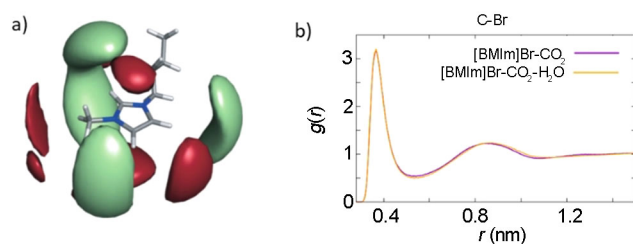
Figure 3. Molecular dynamics simulations (MDS) involving ILs and CO_2. a) Spatial distribution functions (SDFs) for the PF_6 anion (green) and CO_2 (red) near the imidazolium cation for the interaction of CO_2 with 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF_6) IL (adapted from Corvo et al.[32]) b) Radial distribution functions (RDFs) corresponding to systems containing IL ([BMIm]Br), CO_2, and H_2O. C(CO_2)-Br(anion) (adapted from Simon et al.[34]).

3. CO₂ in Basic ILs

In the case of ILs containing basic anions such as acetate, imidazolate, and triazolate, the situation is far from clear. It is usually assumed that there is a covalent interaction of CO_2 either with the cation or the anion, hence absorbing and activating 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 CO_2, and reduce the overpotential for CO_2 reduction.[38] The activation of CO_2 in these cases is probably caused by the breaking of the CO_2 linearity geometry, and in electroreductions, it is also assumed to be attributable to the stabilization of the CO_2 radical anion ($CO_2^{\bullet-}$) provided by the cation (usually imidazolium).[15,29,39] 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.[40,41]
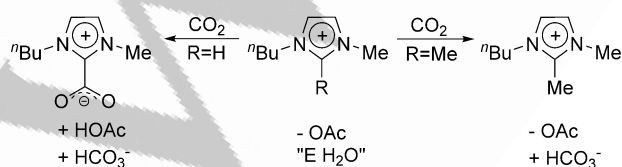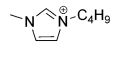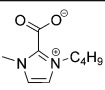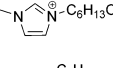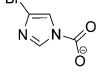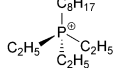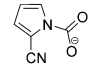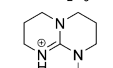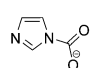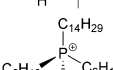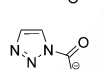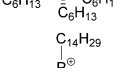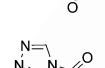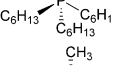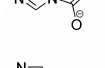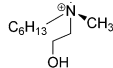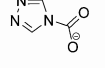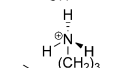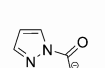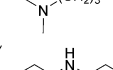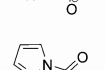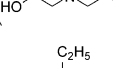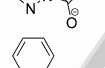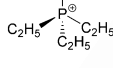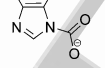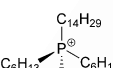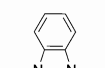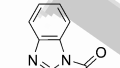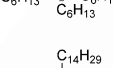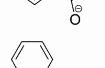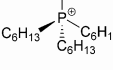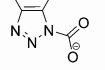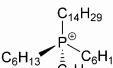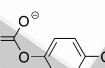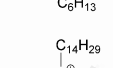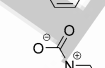

Scheme 1. Products from the interaction of "wet" [BMIm][OAc] and [BMMIm][OAc] with CO_2.
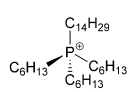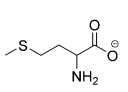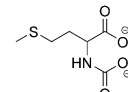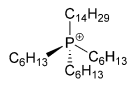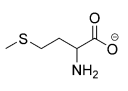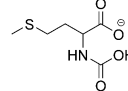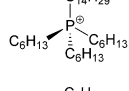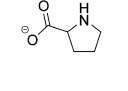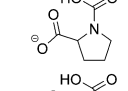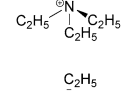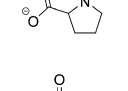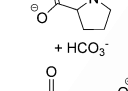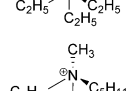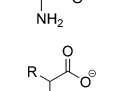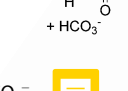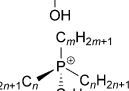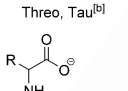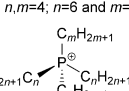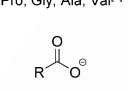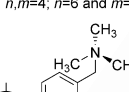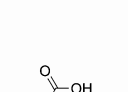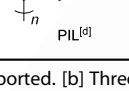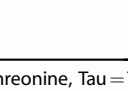
However, in most of these cases, it is claimed that basic (and even super-basic) anions perform a nucleophilic attack on CO_2. These claims are based mainly on the single evidence provided by the presence of a signal at around 158–164 ppm in the ^{13}C NMR spectra of the reaction mixture after CO_2 sorption, 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 CO_2 with ILs containing basic anions is of paramount importance for the design of more effective materials for CO_2 capture, activation, and transformation. Analysis of the published data on the interaction of 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 CO_2 is carbonate/bicarbonate and not CO_2 covalently attached to the anion.

Table 1 shows the claimed structures of the products resulting from the interaction of CO_2 and ILs containing basic anions and the respective ^{13}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.[42] Only in the case of [BMIm][OAc] ■■please define BMIm.■■ was the structure of the carboxylic–imidazolium product firmly established by a series of techniques (including X-Ray structure).[43] In many cases, only weak evidence was provided for the formation of 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 CO_2 and this pocket water must never be disregarded. Therefore, it is clear that 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).[44]

Controversial results are often found in the literature regarding mixtures between [BMIm][OAc], CO_2, and water.[62–65] Combining NMR analysis and molecular dynamics simulations (MDS), Gomes and co-workers observed the formation of a cation–CO_2 complex resulting from the abstraction of H-2 of the imidazolium cation in mixtures between [BMIm][OAc] and CO_2.[33] Additionally, a signal around 160 ppm was detected in the ^{13}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 H_2O 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_2 with ILs containing basic anions.

Entry	Cation	Anion	CO_2 product (attributed by the authors)	COO— shift [ppm]	Sorption total [mol_{CO_2}/mol_{IL}]	Conditions T [°C]/P [bar]	Ref.
1				160.0	0.95	40/10	[45]
2				161.3	1.60	25/1 (60 cm³ min⁻¹)	[46]
3				ca. 160 (HCO_3^-) ca. 145 (N-CO_2)	0.55 (HCO_3^-) 0.35 (N-CO_2)	25/1	[47]
4				—[a]	1.03	23/1	[48]
5				160.3	0.65	22/50 cm³ min⁻¹ ■■please check. ■■	[49]
6				160.2	0.82	22/1 (50 cm³ min⁻¹)	[49]
7				163.9	1.57	20/1	[50]
8				162.9	0.79	22/1 (50 cm³ min⁻¹)	[51]
9				164.2	0.53	55/1	[52]
10				ca. 160 (HCO_3^-) ca. 150 (N-CO_2)	0.77 (HCO_3^-) 0.18 (N-CO_2)	25/1	[47]
11				160.2	1.20	22/1 (50 cm³ min⁻¹)	[49]
12				160.3	0.23	22/1 (50 cm³ min⁻¹)	[49]
13				158.8	0.82	30/1 (60 cm³ min⁻¹)	[53]
14				166.6 (N-CO_2) 159.3 (O-CO_2)	1.58	20/1	[54]
15				160.0	0.26	–/1	[55]
16				177.6 (N-CO_2) 159.9 (O-CO_2)	1.40	30/1	[56]
17				■■Please check product.■■ 156.8 (O-CO_2) 163.5 (N-CO_2)	1.69	40/1	[57]

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Table 1. (Continued)

Entry	Cation	Anion	CO2 product (attributed by the authors)	COO− shift [ppm]	Sorption total [mol$_{CO_2}$/mol$_{IL}$]	Conditions T [°C]/P [bar]	Ref.
18	[P$_{66614}$] phosphonium (C$_{14}$H$_{29}$, C$_6$H$_{13}$)	methionine anion	carbamate product	160.0	0.93 (0.74 chemical/ 0.19 physical)	25/1	[58]
19	[P$_{66614}$] phosphonium	methionine anion	carbamic acid product	176.0	ca. 1.0[e]	25/1	[59]
20	[P$_{66614}$] phosphonium	prolinate	carbamic acid product	158.4	ca. 1.0[e]	25/1	[59]
21	tetraethylammonium	prolinate	carbamic acid product + HCO$_3$−	162.6 (N–CO$_2$) 159.4 (HCO$_3$)	ca. 1.0[e]	25/1 (flow)	[40]
22	tetraethylammonium	glycinate	carbamic acid product + HCO$_3$−	163.3 (N–CO$_2$) 159.4 (HCO$_3$)	ca. 1.0[e]	25/1 (flow)	[40]
23	C$_5$H$_{11}$, N⁺(CH$_3$), C$_5$H$_{11}$, OH	R-amino acid; Threo, Tau[b]	HCO$_3$−	164.4 (N–CO$_2$) 160.6 (HCO$_3$)	_[a]	25/1 (2.36 cm^3 min^{-1})	[60]
24	phosphonium; C$_m$H$_{2m+1}$, C$_n$H$_{2n+1}$; n,m=4; n=6 and m=14	R-amino acid; Pro, Gly, Ala, Val[c]	HCO$_3$−	161.5	1.01–1.10	25/5	[41]
25	phosphonium; C$_m$H$_{2m+1}$, C$_n$H$_{2n+1}$; n,m=4; n=6 and m=14	R=H,alkyl carboxylate	HCO$_3$−	161.5	0.33–0.50	25/5	[41]
26	H$_3$C, N⁺(CH$_3$), CH$_3$ benzyl polymer; PIL[d]	carbonate / OH	HCO$_3$−	161.0	_[a]	25/1 (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_2 capture and utilization.[47]

Conflicting structural attribution of the products resulting from the interaction between CO_2 and ILs is also evident in the case of prolinate-containing ILs (Scheme 2). Upon association with a tetraalkylphosphonium cation ([P$_{66614}$]) ■■ please define P$_{66614}$·■■ a product resulting from the nucleophilic attack of the amine by CO_2 was proposed on the basis of IR studies, but the reported ^{13}C NMR indicated quite a higher-field ^{13}C chemical shift (158.4 ppm) than would be expected for such a structure,[59] which is in the expected range for a bicarbonate.[40] In the case of the prolinate associated with the imidazolium cation and the atmospheric pressure sorption of CO_2, three main products were observed by ^{1}H and ^{13}C NMR spectroscopy: bicarbonate, proline, and CO_2-prolinate adduct (Scheme 2).[34]

A similar idea can be extended to other amino-acid-based ILs. Recently, CO_2 absorption in anion aqueous solutions (50 wt%) of tetraalkylammonium-based ILs with threonine (Threo) and taurine (Tau) was studied by liquid- and solid-state ^{13}C NMR and ^{15}N magic-angle spinning NMR spectroscopy.[60] A precipitated product formed by the reaction with CO_2 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.[66]

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_2–imidazolate adduct was claimed upon interaction with CO_2, again on the basis of ^{13}C NMR data and on the signal intensity corresponding to the carbonyl group increases upon addition of water;[49] in this case, again, the ^{13}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_2 generates bicarbonate and not

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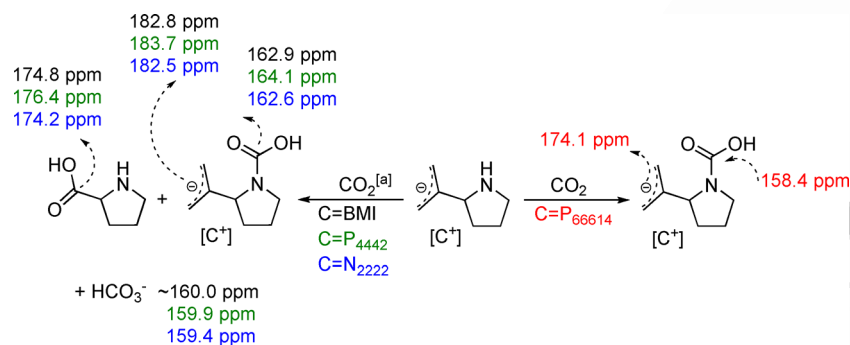
Scheme 2. Reported structures of the products resulting from the interaction of CO_2 with prolinate associated with imidazolium and phosphonium cations (adapted from Simon et al.[34]).
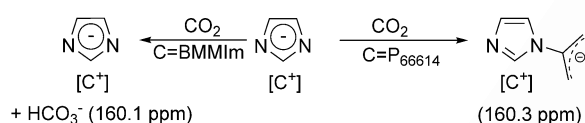
Scheme 3. Proposed structures for the interaction of CO_2 with ILs associated with the imidazolate anion. [a] Depending on experimental parameters: CO_2 pressure, quantity of water, and pH of solution.

any anion–CO_2 adduct, as demonstrated by a series of homo- and heteronuclear NMR experiments.[44]

More intriguing results were reported on the use of imide-based ILs that display an impressive gravimetric CO_2 capacity (up to 22 wt%), namely tri-*n*-butyl-ethyl-phosphonium (P_{4442})-based ILs associated with diacetamide (DAA) and succinimide (Suc) anions.[67] Through a combination of quantum chemical calculations, FTIR spectroscopy, and ^{13}C NMR investigations involving the cooperative interactions between CO_2 and multiple active sites of the preorganized anion, a mechanism has been proposed (Scheme 4). The authors also reported CO_2 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_2. In the ^{13}C NMR spectra, a new signal was observed around 159 ppm, attributed to the N—CO_2 interaction, and a shift in the C=O signal of the anions from 195.6 to 188.0–182.8 ppm.[68] 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_2.[69]

Recently, in the same context, a strategy to improve CO_2 capture by reducing cation–anion interactions in 2-hydroxyl
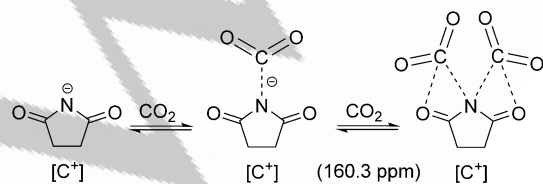
pyridium (2-Op) anion-based ILs was reported. The ^{13}C NMR spectrum of [P_{4442}][2-Op] after the sorption of CO_2 showed two new signals at 177.6 and 159.9 ppm. The authors attributed the signals to the N and O sites of the [2-Op] anion, cooperatively bound to a CO_2 molecule, respectively.[56]

The products obtained using ILs with pyrrolide-based anions for CO_2 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 ^1H NMR data; however, no reports of the ^{13}C NMR chemical shift have been found.[70,71] 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_2 (Scheme 5). They suggest that in mixtures of ILs + CO_2 + H_2O, the anion is reprotonated, thus leaving CO_2 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_2 and N of the anion (2-cyanopyrrolide) was also confirmed by the appearance of a new signal around 145 ppm.[47]

It is quite intriguing that most reports related to the sorption of CO_2 with ILs associated with basic anions assumed the covalent interaction of CO_2, 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.[18] The acidity/basicity of these ILs is, therefore, quite dependent upon the amount of water, and the determination of the pH of IL

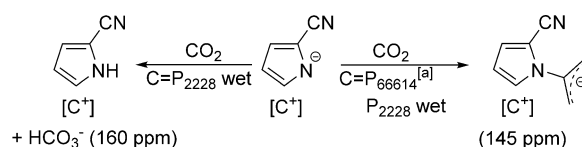**Scheme 4.** Proposed structures for the interaction of CO_2 with IL containing succinimide anion (adapted from Huang et al.[67]).


Scheme 5. Proposed structures for the interaction of CO_2 with ILs associated with the 2-cyanopyrrolide anion. [a] Chemical shift not reported.

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solutions in organic solvents such as MeCN and DMSO is highly important in the presence of "dissolved" CO_2, in particular for electrochemical reductions[38] and chemical reductions.[13] For example, the buffering properties of [BMMIm][OAc] have been used to promote the selective hydrogenation of CO_2 to free formic acid.[8,9] Moreover, IL/DMSO/H_2O solution behaves as a buffer-like solution favoring the formation of bicarbonate, which, in turn, provides a constant supply of dissolved CO_2 necessary for the electrochemical reduction to occur efficiently, facilitating the diffusion of CO_2 to the surface of the electrode.[72] Furthermore, there are clear effects of bicarbonate buffer concentration on the partial currents of the major products formed by reduction of CO_2 over Cu electrodes. The composition and concentration of electrolyte anions have relatively little effect on the formation of CO, HCOO, C_2H_4, and CH_3CH_2OH, but have a significant effect on the formation of H_2 and CH_4.[73]

The interaction of CO_2 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_a than H_2O, can activate the water by abstraction of a hydrogen atom to yield hydroxide and a protonated anion, followed by reaction with CO_2 to form bicarbonate/carbonate.
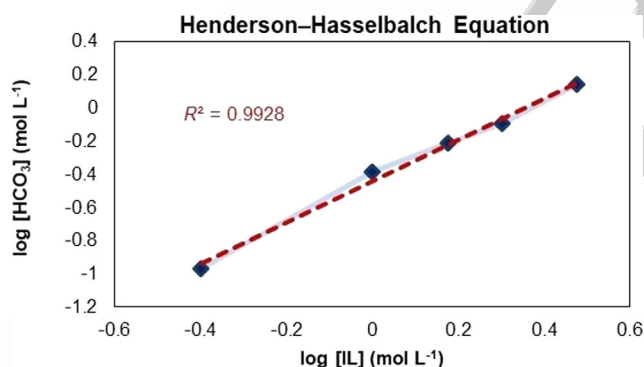
Figure 4. Example of the typical buffer-like properties of ILs upon interaction with CO_2 (double log of [BMMIm][Im] solutions in DMSO/H_2O, 95:5). Adapted from Gonçalves et al.[29]
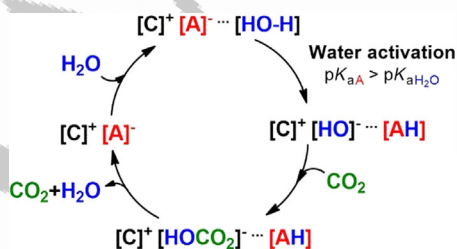
Scheme 6. Pathway of bicarbonate formation in bare ILs with basic anions.

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.[74,75] Despite the drying procedures adopted, the IL water content is always significant and able to create a ternary system (CO_2 + 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_2 dissolution); and 3) enhancement (the presence of water promotes the CO_2 chemical sorption).[76] The reaction pathways of the interaction of CO_2 with ILs containing basic anions probably involves the rapid physical sorption of CO_2, which is almost instantaneously transformed into bicarbonate/carbonate, and this new basic IL solution promotes the reaction of cations and/or anions with CO_2, forming new IL adducts. In particular, 1,3-dialkylimidazolium can generate carbenes and the carboxylate adduct, which can act as a CO_2 transferring agent to other substrates present in the medium.[77]

The ^{13}C NMR chemical shift of the CO_2 adducts with imidazolium cations generally appears at approximately 155 ppm.[34] The reaction between CO_2 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_3^- is generally reported between 159–161 ppm in ^{13}C NMR spectra. Moreover, it may appear at higher chemical shift (163–167 ppm) in systems with higher pH (equilibrium toward CO_3^{2-}).[78] Finally, to assign the structure of the CO_2–IL adducts unambiguously■ ■ok?■ ■, it is important to perform multinuclear NMR experiments, with the use of ^{13}C-enriched compounds (at least ^{13}C-enriched CO_2, in FTIR and mass spectrometry). The formation of bicarbonate can be confirmed easily by using $^{13}CO_2$ and D_2O and performing ^{13}C and 2D multinuclear NMR experiments such as HMBC, HSQC, and HOESY experiments.[32,34,40,44,47,64,79,80]

4. Conclusions

Ionic liquids (ILs) containing basic anions such as carboxylates, N-heterocycles, and amino acids have been used extensively for CO_2 capture. ^{13}C NMR and IR spectroscopy are the most common techniques applied to study the ILs–CO_2 sorption mechanisms. The ^{13}C chemical shifts of the CO_2 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_2 gas should not be ignored as it directly affects the gas solubility and CO_2 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_2, the formation of bicarbonate/carbonates should be considered as possible activation/reaction pathways. Such species can be used as CO_2-active intermedi-

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

Conflict of interest

The authors declare no conflict of interest.

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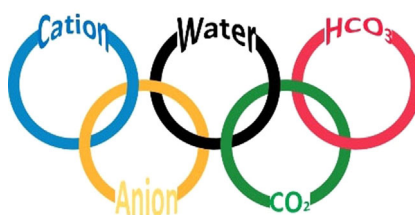Chemistry
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M. Zanatta, N. M. Simon,* J. Dupont*

■■ – ■■

The Nature of Carbon Dioxide in Bare Ionic Liquids

Acid-base Games

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