

CO₂ in 1-Butyl-3-methylimidazolium Acetate. 2. NMR Investigation of Chemical Reactions

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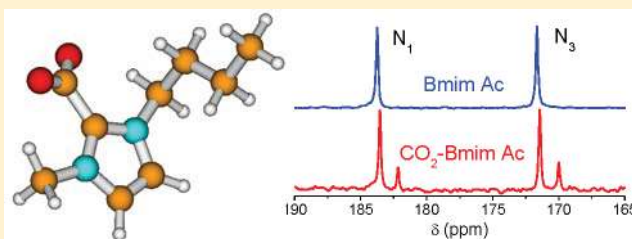
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S Supporting Information

ABSTRACT: The solvation of CO₂ in 1-butyl-3-methylimidazolium acetate (Bmim Ac) has been investigated by ¹H, ¹³C, and ¹⁵N NMR spectroscopy at low CO₂ molar fraction (mf) (x_{CO_2} ca. 0.27) corresponding to the reactive regime described in part 1 of this study. It is shown that a carboxylation reaction occurs between CO₂ and Bmim Ac, leading to the formation of a non-negligible amount (~16%) of 1-butyl-3-methylimidazolium-2-carboxylate. It is also found that acetic acid molecules are produced during this reaction and tend to form with elapsed time stable cyclic dimers existing in pure acid. A further series of experiments has been dedicated to characterize the influence of water traces on the carboxylation reaction. It is found that water, even at high ratio (0.15 mf), does not hamper the formation of the carboxylate species but lead to the formation of byproduct involving CO₂. The evolution with temperature of the resonance lines associated with the products of the reactions confirms that they have a different origin. The main byproduct has been assigned to bicarbonate. All these results confirm the existence of a reactive regime in the CO₂–Bmim Ac system but different from that reported in the literature on the formation of a reversible molecular complex possibly accompanied by a minor chemical reaction. Finally, the reactive scheme interpreting the carboxylation reaction and the formation of acetic acid proposed in the literature is discussed. We found that the triggering of the carboxylation reaction is necessarily connected with the introduction of carbon dioxide in the IL. We argue that a more refined scheme is still needed to understand in details the different steps of the chemical reaction in the dense phase.



I. INTRODUCTION

In a recent study (part 1), we have investigated by Raman spectroscopy the dense phase of the mixture of carbon dioxide in 1-butyl-3-methylimidazolium acetate (Bmim Ac) in a large concentration range (x_{CO_2} molar fraction (mf) up to 0.49) at 313 K.¹ We have shown that two distinct solvation regimes occur. The first one, corresponding to CO₂ concentration extending to ca. 0.35 mf, was found to be characterized by sizable perturbations of the ionic liquid (IL) and by the absence of the strongly active CO₂ Fermi dyad always observed for this molecule diluted in organic or ionic liquids.^{2–4} We came to the conclusion that carbon dioxide reacted with the cation, leading to the carboxylation of the imidazolium ring and concomitantly to the formation of acetic acid. In the course of these studies, we also found that the Raman spectra performed on diluted CO₂–Bmim Ac mixture ($x_{\text{CO}_2} < 0.25$) did not evolve with time

even after a 6 month period, indicating that the carboxylation reaction is irreversible. In contrast, the second regime ($x_{\text{CO}_2} > 0.35$) was found to be characterized by a very weak perturbation of Bmim Ac compared to the differences detected in the first regime and by the observation of the carbon dioxide Fermi dyad, showing that the reaction has been strongly moderated. It has been interpreted as resulting from the interaction of the nascent acetic acid with the oxygen atom of the acetate group involved in a single interaction with the proton bonded to the C₂ atom of the imidazolium ring (see Figure 1). The detection of the Fermi dyad shows that CO₂ interacts in the second regime in a softer way with the variety of

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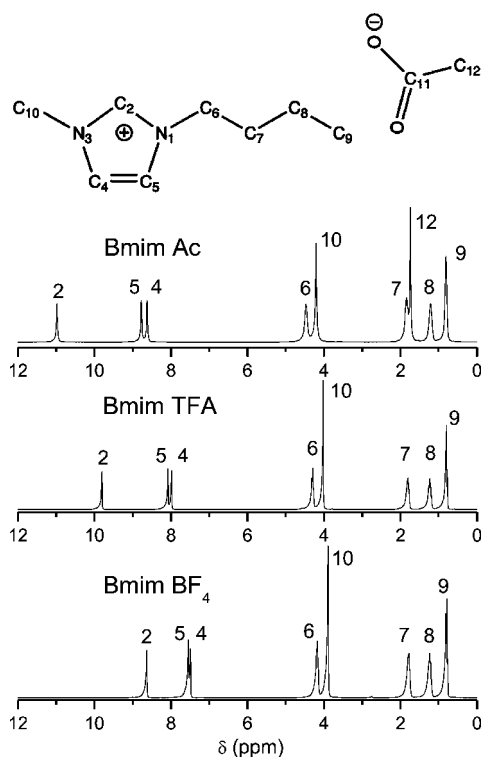


Figure 1. ^1H NMR spectra of Bmim BF_4 , Bmim TFA, and Bmim Ac. The schematic representation of the Bmim Ac ion pair with the labeling of the carbon atom used in the assignment is displayed.

species (ions pairs, carboxylate molecules, acetic acid and CO_2) resulting from the reaction. The nature of the interactions has been assessed by DFT modeling showing that CO_2 , in an almost linear structure, interacts preferentially with the COO groups of the acetate anions and of the carboxylate molecules.¹ This behavior is markedly different from that we reported for CO_2 mixed in the 1-butyl-3-methylimidazolium trifluoroacetate (Bmim TFA) ionic liquid.⁴

From these results, we have been able to argue that the difference between the solubility of CO_2 in Bmim Ac and in Bmim TFA^{5,6} is a consequence of the carboxylation reaction existing in the first regime and of the variety of environments offered to CO_2 in the second regime.

The aim of the current investigation is to further explore at the molecular level, the origin of the unusual high solubility of CO_2 in Bmim Ac observed in the first regime. For this reason, we will mostly consider here experiments performed at low pressure typically at 0.1 MPa and 298 K for which the CO_2 solubility is as high as 0.27 mf. This solubility value proves to be convenient from the experimental ground as it ensures that the current studies will be always performed in the first solvation regime. In a recent communication, experimental evidence has been obtained from the X-ray structure of the solid-state products resulting from the reaction of CO_2 with acetate ionic liquids in particular the 1-ethyl-3-methylimidazolium acetate.⁷ These authors also characterized by ^1H and ^{13}C NMR spectra the adduct products of a chemisorption obtained bubbling CO_2 through the IL. In a very recent letter, we have also reported evidence on the formation of 1-butyl-3-methylimidazolium-2-carboxylate in the mixture of CO_2 with 1-butyl-3-methylimidazolium acetate under mild conditions (298 K, 0.1 MPa) in the liquid phase using Raman and NMR (^1H , ^{13}C , and ^{15}N) spectroscopy and DFT calculations.⁸ This preliminary study

showed that the main features observed in the liquid mixture (carboxylate and acetic acid formation) are also observed in the solid state. Our aim now is to investigate in depth the existence of the carboxylation reaction proposed in our former investigation and in particular, the triggering of the carboxylation reaction by CO_2 . Furthermore, we want to assess the consequence of the acetic acid formation which has been put indirectly in evidence in our previous Raman study.

We have also addressed here the issue concerning the influence of water traces on the carboxylation reaction.⁵ As far as we know, its role in assisting this reaction has been evoked but never discussed in depth at the molecular level.^{5,7} Therefore, a complete characterization of the products formed in the CO_2 -Bmim Ac- H_2O system remains to be done and is aimed at the current study. This investigation led us to characterize the byproduct formed due to the water presence and how their formation can compete with the carboxylation reaction.

II. EXPERIMENTAL SECTION

II.1. Experimental Details. The ionic liquids Bmim Ac, Bmim TFA, 1-butyl-3-methylimidazolium tetrafluoroborate (Bmim BF_4 , purity >98%) originated from Solvionic, the CO_2 from Air Liquide (purity 99.995%), and the ^{13}C labeled CO_2 from Aldrich (99 at. %). Additional glacial acetic acid (Riedel-de Haën, >99.8%), sodium hydrogenocarbonate (Aldrich, >99.5%), sodium carbonate (Aldrich, 99.995%), and heavy water (Aldrich, >99.990) were used without further purification. The ILs were put in a glass container connected to a vacuum line and dried at 353 K under a primary vacuum during more than 48 h, with a continuous stirring performed with a magnetic rotating agitator. The water content was measured by Karl Fischer titration and found to be 530 ppm, much lower than the value measured for the undried ionic liquid (~5000 ppm). Carbon dioxide was then introduced under a 0.1 MPa pressure in the Bmim Ac and the solution was stirred for a further period of about 30 h. After the container with the mixture under its vapor pressure was isolated, a Raman spectrum was taken to check for the presence of the strong perturbations observed in the spectral domain 1200–1800 cm^{-1} and the absence of the characteristic dyad of CO_2 that we have reported in the Raman study, ensuring that the first solvation regime was reached.¹ Then, the mixture was transferred into a standard NMR glass tube (5 mm inner diameter) and tapped with an inner Teflon cap and the standard outer plastic tap. Parafilm was subsequently used to isolate the extremity of the tube. This sealing method was used to avoid any contact with the atmosphere. During the very short time corresponding to the filling of the tube under the atmosphere, we did not observe any bubbling of the liquid, thus excluding a degassing of CO_2 from the liquid phase. The integrity of the solution prepared using this protocol was checked by further comparative Raman measurements. We emphasize that the NMR spectra of the samples did not evolve in time as seen from the comparison of the spectra recorded for fresh solutions, just after filling the tube, with those measured at regular interval periods during more than 6 months at the exception of the resonance line assigned to the acetic acid (see section III).

A number of CO_2 -Bmim Ac solutions aimed at performing complementary tests have been prepared by keeping the undried IL in a stainless steel vessel in which carbon dioxide (at pressure ca. 6 MPa) was introduced at 298 K. After the mixture

Table 1. ^1H NMR and ^{13}C NMR Chemical Shifts (δ , ppm) of the Pure 1-Butyl-3-methylimidazolium Acetate (Bmim Ac) and of the Solution Obtained by Mixing CO_2 with Bmim Ac at 298 K under 0.1 MPa^a

atom	Bmim Ac		CO_2 -Bmim Ac				Bmim TFA	
	^1H	^{13}C	^1H	^1H secondary lines	^{13}C	^{13}C secondary lines	^1H	^{13}C
9	0.72	13.10 (124)	0.72		13.10 (125)	13.25 (124)	0.84	12.69 (125)
8	1.13	19.14 (126)	1.13		19.16 (127)	19.32 (125)	1.27	19.04 (126)
12	1.64	25.53 (124)	1.69		24.81 (125)			114.7 116.7 (298) 118.7 120.6
7	1.74	32.22 (128)	1.75		32.13 (128)	32.88 (127)	1.84	31.94 (127)
10	4.11	35.49 (143)	4.08	4.13	35.43 (143)	36.65 (143)	4.06	35.47 (143)
6	4.37	48.54 (143)	4.35	4.60	48.54 (143)	48.8 (138)	4.33	49.05 (143)
4	8.52 ^d	124.1 ^d (204)	8.36	8.31	124.2 (204)	123.4 (204)	8.00	122.7 (204)
5	8.67 ^d	123.1 ^d (204)	8.51	8.40	123.1 (204)	122.2 (204)	8.10	124.0 (202)
2	10.88	138.6 (220)	10.67		138.9 (222)	141.6	9.79	137.8 (222)
11		175.1			174.7			159.8 160.0 (32) 160.2 160.4
	COO^b					155.3		
	COOH^c			15.95–12.3 ^e				

^aThe ^1H NMR and ^{13}C NMR chemical shifts measured in this work for pure 1-butyl-3-methylimidazolium trifluoroacetate (Bmim TFA) are displayed for comparison. The coupling constants J (Hz) are given in parentheses. ^b COO group of the carboxylate formed upon the reaction. ^c COOH group of the acetic acid formed upon the reaction. ^dThe assignment of these lines is supported by the 2D ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC NMR sequences (Supporting Information). ^eThe position of this resonance line evolves from 15.95 ppm (3 days) to 12.3 ppm (40 days after preparation of the mixture).

was allowed to equilibrate for at least 2 h, the cell was opened and the pressure released to 0.1 MPa. The mixture was then immediately transferred in a NMR tube sealed as described above. NMR measurements have shown that the solutions prepared that way led to spectra displaying the same relevant line signatures as those prepared under the controlled conditions previously described. The molar fraction of CO_2 in the mixtures at 298 K and under 0.1 MPa has been deduced from data reported previously⁵ and corresponds to a CO_2 concentration of ca. 0.27 mf.

The NMR measurements were performed on Bruker AVANCE III spectrometer operating at 600 MHz Larmor frequency for ^1H , 150 MHz for ^{13}C and 60 MHz for ^{15}N (France). The ^1H spectra were collected after a 30° pulse with a 90° pulse (t_{90}) of 8 μs . The number of scans was ranging from 512 to 1024 with a relaxation delay (d1) of 1 s. The ^{13}C spectra were acquired after a $t_{90} = 15 \mu\text{s}$ and d1 = 3 s. The ^{13}C proton decoupled spectra were measured using the standard WALTZ-16 decoupling sequence. These measurements have been completed by performing 2D ^1H - ^1H COSY, ^1H - ^1H NOESY, ^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC, and ^1H - ^{15}N HMBC sequences. The mixing time for the 1H-1H-NOESY was 750 ms. Finally, 2D ^{13}C - ^1H HOESY and ^{13}C - ^{13}C INADEQUATE sequence on the AVANCE II 400 MHz with a BBO probe at 400 and 100 MHz for ^1H and ^{13}C (France) have been performed. The mixing time for the 13C-1H-HOESY was 900 ms.

Measurements were also performed in a Bruker AVANCE II spectrometer at 300 MHz Larmor frequency for ^1H , 75 MHz for ^{13}C (Portugal). The ^1H spectra were recorded after a single pulse, $t_{90} = 14 \mu\text{s}$ and d1 = 5 s. The number of scans has been ranging from 512 to 1024. The ^{13}C spectra have been acquired after a single pulse with $t_{90} = 11 \mu\text{s}$ and d1 = 3 s. The ^{13}C

proton decoupled spectra was measured using the standard WALTZ-16 decoupling sequence. The samples were contained in standard 5 mm tubes filled with an external lock solvent of D_2O and calibrated with the H_2O signal at 4.8 ppm. The temperature of the samples was regulated and stabilized to within ± 0.5 K using gas flow.

II.2. Results. Assignment of the NMR Spectra of Pure Bmim Ac and Bmim TFA. On Figure 1, we compare the ^1H spectra measured for pure Bmim Ac with that of pure Bmim BF_4 whose assignment is well-known.^{9–11} Moreover, the ^1H spectrum of pure Bmim TFA that has been recently reported is displayed on this figure.¹² Thus, it becomes a simple matter to assign from this comparison the peaks belonging to the Bmim cation common to the three compounds and from the difference between the spectra of Bmim Ac and Bmim TFA the peaks belonging to the acetate anion. The assignment of the protons of Bmim Ac is reported in Table 1 according to the labeling displayed in the schematic drawing of the molecule (Figure 1). In a second step, we have assigned the observed lines of the ^{13}C spectra in natural abundance (Figure 2) using the standard NMR approach, combining two observations: their splitting in multiplets (clearly resolved at 600 MHz in the proton nondecoupled spectra) and their disappearance under the condition of proton decoupling. The labeling of the carbon atom is displayed according to the convention of Figure 1. The chemical shifts corresponding to the ^1H and ^{13}C spectra are reported in Table 1 and their assignment was confirmed from 2D ^1H - ^1H COSY, ^1H - ^{13}C HSQC, and ^1H - ^{13}C HMBC NMR sequences (Supporting Information). We note that the assignment proposed here for ^1H and ^{13}C spectra of pure Bmim Ac is in a very good agreement with that recently reported.¹³ Moreover, a good agreement is obtained for the ^1H spectra of BmimAc¹⁴ and of BmimTFA¹² as well as for the ^{13}C

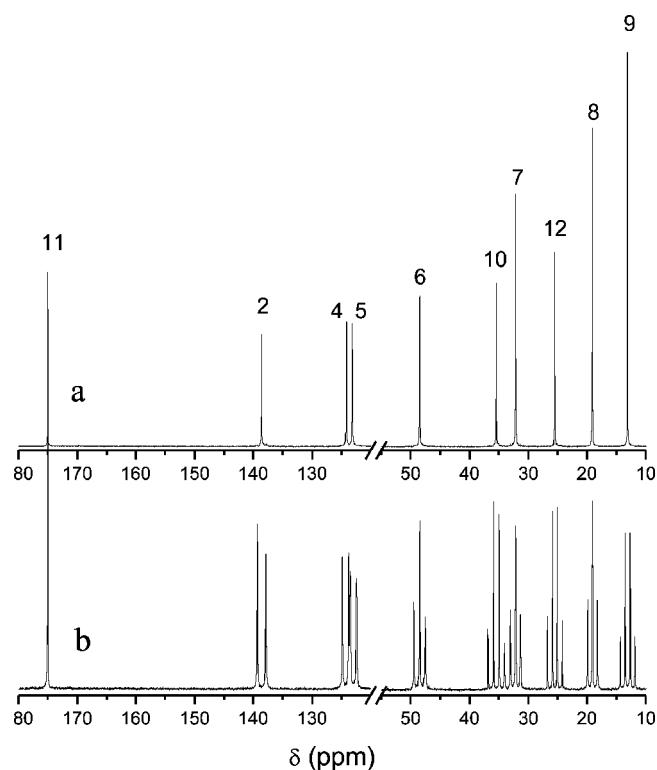


Figure 2. ^{13}C NMR spectra of Bmim Ac with (a) and without (b) proton decoupling.

spectrum of Bmim Ac,¹⁴ although the chemical shifts values that we have obtained are systematically slightly greater.

NMR Spectrum of the CO_2 -Bmim Ac Mixture. The proton decoupled ^{13}C spectrum of the CO_2 -Bmim Ac mixture having a CO_2 molar fraction close to ca. 0.27 is displayed in comparison with that of the pure IL (Figure 3). From this comparison, two main observations can be readily made. A new line centered at ca. 155 ppm is observed having no counterpart in the spectrum of the pure IL. In addition, the main intense lines of Bmim Ac are accompanied by secondary lines of lower intensity (as well as in the ^1H spectrum) (Table 1 and Supporting Information). The origin of the new peak is clearly connected with carbon dioxide. However, the isolated CO_2 has a single resonance line situated at 125.4 ppm,¹⁵ and therefore the new peak, although correlated to the presence of this molecule, cannot correspond to the spectral signature of the CO_2 solvated in the IL. Therefore, we may conclude that CO_2 has reacted with the IL. In our previous investigation, we have put in evidence the existence of an irreversible chemical reaction occurring between the carbon dioxide and the Bmim cation to form a carboxylate species.¹ For this purpose, we have proposed a reactive scheme in which CO_2 triggers the carboxylation reaction through two concerted mechanisms which are respectively an isomerization process (chemical exchange of the acidic proton between the imidazolium ring and the acetate anion) and the formation of a “transient” CO_2 -carbene (1-butyl-3-methylimidazole-2-ylidene carbene) complex (Figure 4).

In step 1, the carbon atom of CO_2 is transiently “bonded” to the imidazolium ring after the release of the proton of carbon 2 of the ring. Such a concerted mechanism takes place on a very short time scale (subpicosecond range) during which the deprotonated C_2 site can be considered as a “carbene” species,

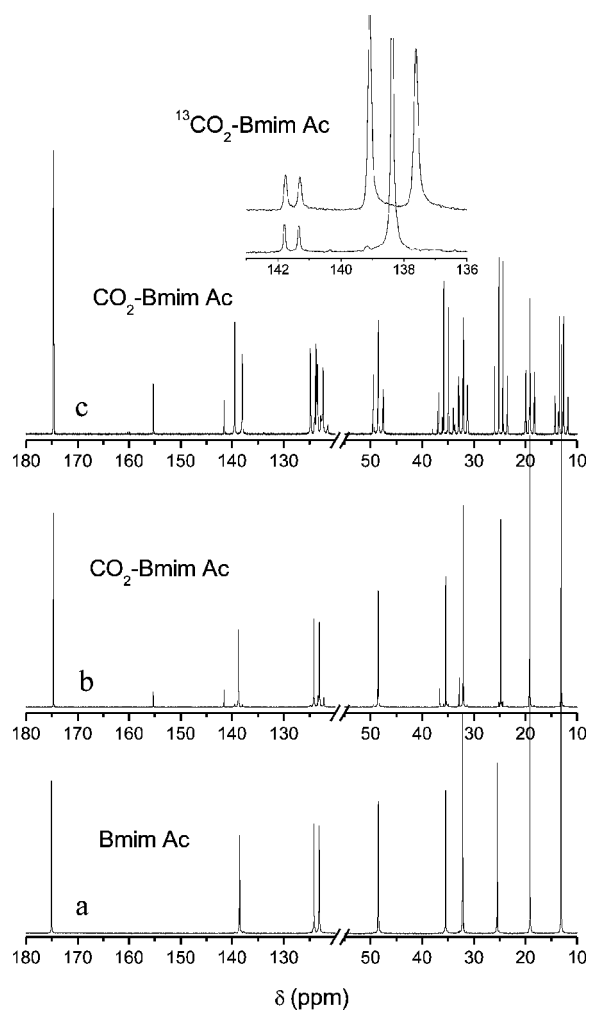
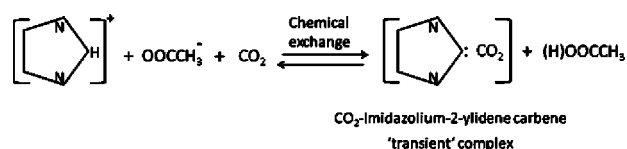


Figure 3. Comparison of (a) proton decoupled ^{13}C NMR spectrum of pure Bmim Ac, with (b) proton decoupled and (c) proton nondecoupled spectra of the CO_2 -Bmim Ac mixture. The inset corresponds to a magnification of the spectra in the region of carbon 2 of the $^{13}\text{CO}_2$ -Bmim Ac mixture. In all these experiments, the CO_2 molar fraction is about 0.27.

Step 1



Step 2

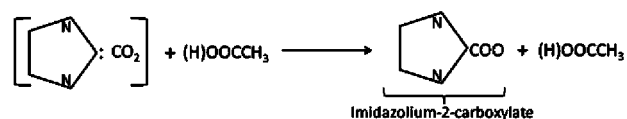


Figure 4. Concerted mechanisms for the formation of 1-butyl-3-methylimidazolium-2-carboxylate involving the isomerization process and the formation of a “transient” CO_2 -carbene complex.

avoiding to suppose the formation of a long-lived carbene entity, questionable in dense phase. Then, such a “transient” CO_2 -carbene association can be considered as an intermediate

precursor leading toward a definitive CO₂ capture by imidazole-2-ylidene carbene species (step 2 of the reaction).

If this reaction occurs and is not total, we should expect that the spectrum is a composite one resulting from the addition of the spectrum of the Bmim Ac and of the carboxylate species. In that case, we should detect in the vicinity of each main resonance lines of the IL, secondary lines of lesser intensity corresponding to the carboxylate. This is exactly what can be observed on the ¹³C spectra presented in Figure 3 and also on the 2D ¹H–¹³C HSQC and ¹H–¹³C HMBC NMR sequences (Supporting Information). To ground firmly this conclusion, we have measured the ¹⁵N spectra of pure Bmim Ac and of its mixture with carbon dioxide (Figure 5a,b). In the pure IL, this

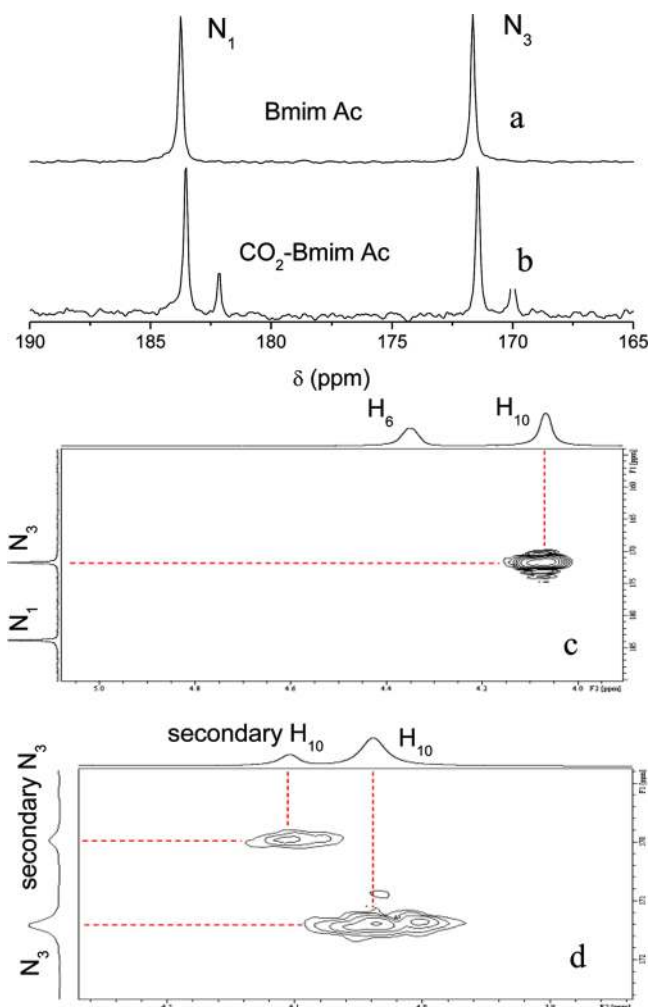


Figure 5. Comparison of the spectra of the pure Bmim Ac (with that of the CO₂-Bmim Ac mixture): ¹⁵N NMR (a) and (b); 2D HMBC ¹H–¹⁵N NMR sequence (c) and (d).

spectrum presents two intense resonance lines centered at about 183.7 and 171.6 ppm assigned to the nitrogen atoms of the ring core. The assignment of these lines is supported by 2D ¹H–¹⁵N HMBC NMR sequence which shows that the proton bonded to carbon atom 10 is correlated with the nitrogen atom N₃ (Figure 5c). We note that this assignment is different with that reported in the literature.¹⁶ In the mixture, two additional resonances lines flanking each of the previous peaks are observed at 182.1 and 170.0 ppm, respectively (Figure 5b), and confirmed by the 2D ¹H–¹⁵N HMBC NMR sequence (Figure

5d). The proportion of the new species estimated from the integrated intensity of the secondary lines of the cation in ¹H, ¹³C and ¹⁵N NMR spectra is about 0.16 molar fraction. This result confirms that the addition of carbon dioxide to the IL leads to the formation of a carboxylate molecule. This finding also supports our previous conclusion concerning the origin of the observed secondary lines.

Having shown that the carboxylation reaction occurs, we may wonder about the favored chemical site among the three possible carbons 2, 4, and 5 of the cation ring. A first answer to this question is provided by the comparison of the decoupled versus non decoupled ¹³C spectra in natural abundance in the mixture in the region of carbon 2 (Figure 3b,c). On the nondecoupled spectrum, the doublet line characteristics of the resonance of carbon 2 (C₂) is observed at about 137.6 and 139.0 ppm and is accompanied by a single line at about 141.6 ppm. Upon proton decoupling, we notice as expected that the doublet line give rises to a singlet (at about 138.3 ppm) whereas the other line is not affected by the decoupling. Clearly, the structure of the doublet line is indicative of the existence of the scalar interaction between the spin of C₂ of the Bmim cation and the spin of the bonded proton. Therefore, this doublet can be assigned to the Bmim Ac species that have not reacted with carbon dioxide. In contrast, the observation of a single line not affected by the proton decoupling reveals the existence of a molecular species in which C₂ is not bonded to a proton as expected for the carboxylate. Such an analysis is confirmed by considering the spectrum of the mixture with labeled carbon dioxide ¹³CO₂. Indeed, we observed on the ¹³C spectrum a doublet centered at about 141.6 ppm that is not affected by the proton decoupling (Figure 3, top). The doublet structure can be therefore interpreted as the signature of the scalar interaction of the spin of C₂ (in natural abundance) with the spin of the labeled carbon atom of the bonded carbon dioxide. A final piece of evidence has been provided by measuring the 2D spectrum using the INADEQUATE sequence (Figure 6). It appears immediately that the peak of

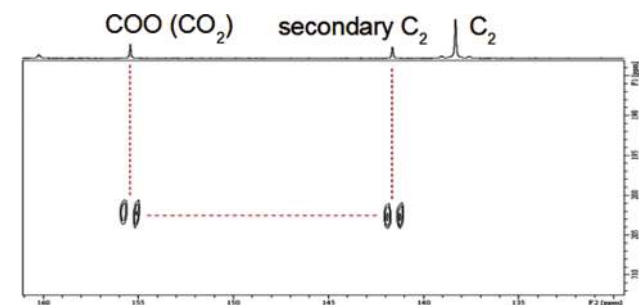


Figure 6. 2D NMR spectrum obtained from the INADEQUATE sequence on the ¹³CO₂-Bmim Ac mixture: the correlation observed between the C atom of the bonded CO₂ of the new species (155.3 ppm) and the C₂ atom (141.6 ppm) proves that these carbon atoms are covalently bonded.

the C₂ of the Bmim cation (138.3 ppm) is not correlated with the two new peaks situated at 155.3 and 141.6 ppm. In contrast, we note that these two latter lines are correlated one to each other showing that a new species is formed in which carbon dioxide is covalently bonded to the C₂ of the imidazolium ring. We can thus conclude that CO₂ reacts spontaneously with the Bmim cation upon mixing to form a carboxylate species, namely a 1-butyl-3-methylimidazolium-2-carboxylate, in which the CO₂

moiety is bonded on C₂. This conclusion is in agreement with the Raman results that we have previously reported.^{1,8} We note that the synthesis of 1,3-dialkylimidazolium-2-carboxylates by direct carboxylation is a subject of a strong current interest.^{17–19} Among the motivation is the use of 1,3-dialkylimidazolium-2-carboxylates in organic synthesis and in synthesis of halogen-free ionic liquids²⁰ or as air- and moisture-stable species to transfer N-heterocyclic carbene (NHC) to a variety of metal salts with release of CO₂.^{21,22} In this context it was found that NHCs freely add CO₂ to form (reversibly under certain conditions) the corresponding imidazolium carboxylate.²³

The synthesis and characterization of 1-butyl-3-methylimidazolium-*n*-carboxylates (with *n* = 2, 4, and 5) using a number of physical–chemical techniques including ¹³C NMR spectroscopy (D₂O solution, 500 MHz) has been reported.¹⁸ The comparison of the chemical shifts of the resonance lines that these authors have reported for the *n* = 2 carboxylate is in a good agreement with those we have measured (Table 2). The

Table 2. ¹³C NMR Chemical Shifts (δ , ppm) of the 1-Butyl-3-methylimidazolium-2-carboxylate Obtained by Mixing CO₂ with Bmim Ac at 298 K under 0.1 MPa Compared with Those Reported in the Literature for 1-bButyl-3-methylimidazolium-*n*-carboxylate with *n* = 2, 4, 5 in D₂O¹⁸

atom	1-butyl-3-methylimidazolium-2-carboxylate ^a	1-butyl-3-methylimidazolium-2-carboxylate ^b	1-butyl-3-methylimidazolium-4-carboxylate ^b	1-butyl-3-methylimidazolium-5-carboxylate ^b
9	13.25	13.08	13.09	13.09
8	19.32	19.16	19.16	19.16
7	32.88	32.27	31.55	32.35
10	36.65	36.88	36.06	36.14
6	48.8	49.57	49.57	49.67
4	123.4 ^c	122.4	131.38	126.66
5	122.2 ^c	123.39	125.26	130.78
2	141.6	140.29	137.53	142.26
COO	155.3	158.15	163.03	163.09

^aThis work. ^bLiterature values.¹⁸ ^cThe assignment of these lines is supported by the 2D ¹H–¹³C HSQC and ¹H–¹³C HMBC NMR sequences (Supporting Information).

peak reported at 158.15 ppm corresponds to the new line observed here at 155.3 ppm and assigned to the carbon atom of the carboxylate group of the 1-butyl-3-methylimidazolium-2-carboxylate. The ¹³C NMR spectra reported for the two other compounds (i.e., 1-butyl-3-methylimidazolium-*n*-carboxylate with *n* = 4 and 5), possess a resonance line at about 163 ppm that is not observed here. Moreover, the chemical shifts of the resonance lines of carbons 4 and 5 for *n* = 4 are respectively 131.4 and 125.3 ppm, whereas these values are 126.7 ppm and 130.8 ppm for *n* = 5, which are clearly different from the corresponding values reported for *n* = 2 (122.4 and 123.4 ppm, respectively) (Table 2). Because these values (for *n* = 2) agree with those obtained in the present work (124.2 and 122.2 ppm), we can conclude that a selective carboxylation of the ring occurred. It is noteworthy that these results justify the point of view of a greater reactivity of site 2 due to the greater acidic character of the proton bonded to this site.

It was established that CO₂ dissolved in imidazolium-based ILs is found preferentially interacting with the anion. The hydrogen bonding of the anion to the “acidic” C₂ proton of the imidazolium ring prevents CO₂ from associating with the

cation.^{24–26} DFT and NMR studies in diluted solutions of 1-ethyl-3-methylimidazolium tetrafluoroborate (Emim BF₄) in dichloromethane showed that the equilibrium existing between the structures in which the anion is located near the C₂ atom of the ring (mainly favored) or close to C₄ or C₅ atoms was found to be influenced by the concentration/polarity of the solvent.²⁷ Moreover, neutron diffraction and molecular simulation studies of 1-ethyl-3-methylimidazolium acetate (Emim Ac) revealed that acetate anions are hydrogen-bonded to the hydrogen atoms of the cation rings (mainly with the proton bonded to C₂).²⁸ The carboxylation reaction observed in the present study marks a great contrast with the general behavior reported for ILs based ionic liquids.

III. DISCUSSION

Carboxylation Reaction. The eventuality of a chemical reaction occurring in CO₂–Bmim Ac mixtures has been first invoked by Maginn et al.²⁹ from NMR results. Such a reaction would proceed according to a two stages process. In a first step, it is assumed that the proton bonded to C₂ of a Bmim cation is transferred to the acetate anion, to form an acetic acid molecule whereas the deprotonated Bmim cation becomes a transient imidazole-2-ylidene carbene species. In a second step, the carbene species reacts with carbon dioxide to lead to the formation of an imidazolium-2-carboxylate. Incidentally, we note that the signature of an isolated carbene has been recently reported by Holloczki et al. in Emim Ac under very stringent thermodynamical conditions (423 K, 1 Pa),³⁰ which are very different from those considered here in the dense phase. The carboxylation reaction has been critically discussed by Shiflett et al.⁵ in their study of the solvation of CO₂ in Bmim Ac. Because the presence of neither the carboxylate nor the acetic acid was put in evidence, these authors concluded that if the reaction occurs, it should be considered as marginal.

In marked contrast, we have shown that an irreversible chemical reaction takes place from the formation of a transient CO₂–carbene species leading to quantifiable amounts of carboxylate species.^{1,8} In our investigations the amount of formed carboxylate species is estimated to be about 16 mol % of the total mixture which is far from negligible. In other words, the introduction of CO₂ in the IL strongly disturbs the existing equilibrium between the Bmim and acetate ions by triggering the carboxylation reaction. Clearly, the detection of acetic acid becomes of importance to discuss the proposed scheme.

Formation of Acetic Acid. The detection of the proton released by the imidazolium ring upon carboxylation is rather delicate as the existence of a “free” proton in solution can only be put in evidence indirectly. For this purpose, we have first measured the proton NMR spectrum of glacial (i.e., highly concentrated acid, purity >99.8%) acetic acid, which displays two resonance lines situated at about 10.74 and 2.06 ppm assigned to the proton of the COOH and CH₃ groups, respectively (Figure 7). To “track” the signature of the proton, we have added increased amounts of glacial acetic acid to Bmim Ac and considered the resonance line of the proton of the COOH group. At low acidic concentration (0.08 mf), an extremely weak and broad feature, which was absent in the spectrum of the pure ionic liquid, is observed at about 16.2 ppm. Upon increasing the acid concentration (0.16 mf), we notice that this feature becomes more pronounced and is slightly upfield shifted by at ca. 0.5 ppm. Clearly the local ordering of the acetic acid is strongly perturbed upon dilution in the IL. This modification of the state of aggregation of

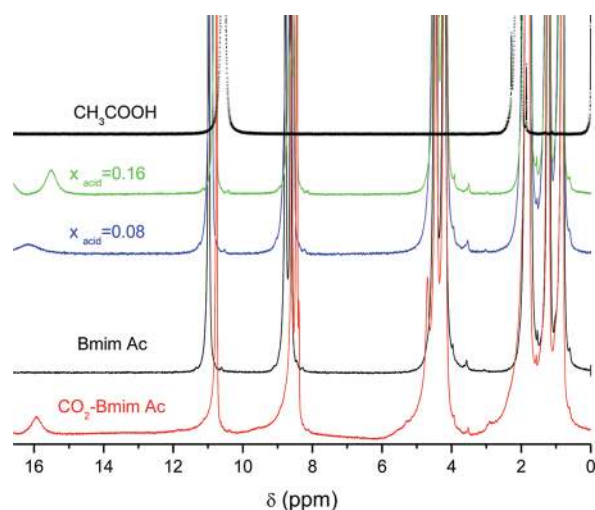


Figure 7. Comparison of the ^1H NMR spectra of acetic acid, mixtures of acetic acid (0.08 and 0.16 acid mf) in Bmim Ac, and pure Bmim Ac (from top to bottom). The spectrum of $\text{CO}_2\text{-Bmim Ac}$ is also displayed for comparison.

carboxylic acids and in particular of acetic acid upon dilution in organic liquids, is well documented.^{31–35} In mixtures with polar solvents, the population of cyclic dimers decreases at the expense of monomers and linear forms that may form complexes with the solvent. This situation occurs as well for acetic acid diluted in Bmim Ac. Let us recall that in Emim Ac the most probable short-ranged local structure consists of anions in which an oxygen atom of the COO^- group interacts in a monodentate configuration with a proton of the imidazolium ring (mainly with the proton bonded to C_2), leaving the other oxygen atom available for other interactions.²⁸ Thus, we may infer that the COOH group of monomers as well as linear dimers of acetic acid molecule interact through hydrogen bond with the available oxygen atom of the COO^- group of nearby acetate anion, whereas the other oxygen atom is hydrogen bonded to the imidazolium ring. Such a proposition is reinforced and attested by both spectral signatures and vibrational DFT modeling.¹

In $\text{CO}_2\text{-Bmim Ac}$, a resonance line not observed in the pure IL, is detected at about 15.95 ppm (Figure 7) and assigned to the COOH group of the acid molecule interacting with “free” atom oxygen atom of the COO group of the ion pair. It was found to correspond to an acidic Bmim solution in which the acid molar fraction is close to 0.12. Therefore, by analogy, we can estimate the molar fraction of nascent acetic acid to be ca. 0.12 in $\text{CO}_2\text{-Bmim Ac}$ solutions. This estimate nicely matches the estimated concentration of carboxylate formed during the reaction as obtained from the ^{15}N spectra. From the previous discussion, we conclude not only that acetic acid molecules are formed in this mixture due to the carboxylation reaction but also that these nascent molecules interact in turn to form the bidentate species discussed before.

A further indirect confirmation of this conclusion can be obtained by considering the ^{13}C resonance line of the methyl groups of the acetate anion of Bmim Ac and of acetic acid, which are detected at 26.1 and 20.8 ppm, respectively (Figure 8). Upon dilution of acetic acid in the IL, the resonance line of the methyl group of the acetate anion shifts progressively upfield with the acid concentration. This trend shows that the methyl group of the anion feels the perturbation of the COO

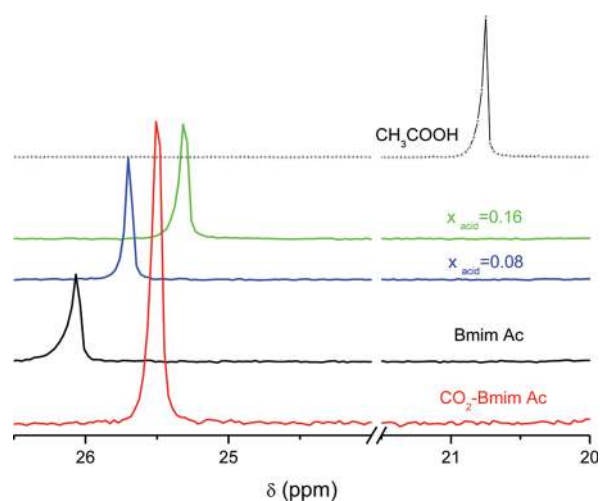


Figure 8. Comparison of the ^{13}C NMR spectra of acetic acid, mixtures of acetic acid (0.08 and 0.16 acid mf) in Bmim Ac and pure Bmim Ac (from top to bottom). The spectrum of $\text{CO}_2\text{-Bmim Ac}$ is also displayed for comparison.

group of the acetate upon their hydrogen bonded interaction with the acid molecules. In $\text{CO}_2\text{-Bmim Ac}$, the resonance line of the methyl group of the acetate anion is centered at about 25.5 ppm and corresponds to the line observed for the mixture Acetic acid–Bmim Ac with an acid molar fraction close to 0.12. We note that this value is close and consistent with those reported previously for the estimated concentration of carboxylate.

All these findings confirm that acetic acid is produced as a consequence of the carboxylation reaction. It should be pointed out that they also support the indirect inference which has been reached in our Raman study concerning the acid production.^{1,8}

A final piece of information has been obtained from the long time evolution of the ^1H spectra of $\text{CO}_2\text{-Bmim Ac}$. We found that the position of the new line observed in ^1H NMR at about 16 ppm changes with time to reach 12 ppm in a 40 day time period (Figure 9). This latter value being close to that observed for pure acid (10.74 ppm) suggests that, with elapsed time, the

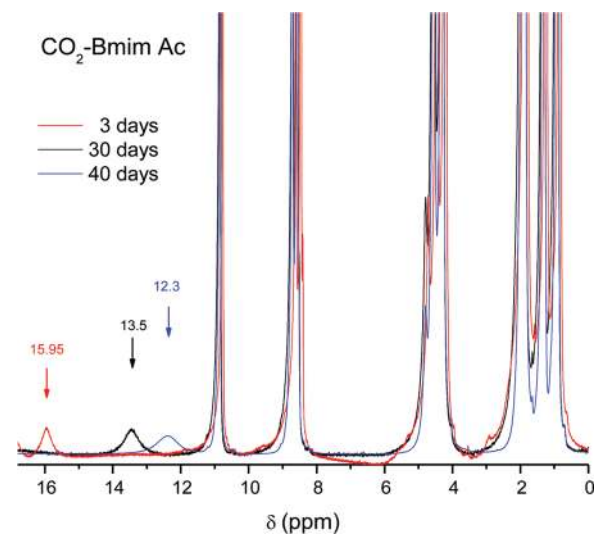


Figure 9. Time evolution of the ^1H NMR spectrum of the mixture $\text{CO}_2\text{-Bmim Ac}$: 3 days (red), 30 days (black), and 40 days (blue) after preparation of the mixture.

acid molecules in CO₂-Bmim Ac tend to form again cyclic dimers mostly existing in the pure acid. This result indicates that the interaction between acetate anion and Bmim cation is slightly more attractive as it is not affected in the same time by a secondary interaction of an acetic acid molecule with the COO group of the anion. Thus, the subtle competition between monodentate and bidentate associations of acetate with Bmim cations (without and with the presence of acetic acid, respectively) leads to favor the former ones (monodentate associations) through a self-association (dimerization) of acetic acid. This dimerization mechanism of acetic acid takes place upon a long time scale (approximately a few days) because the interaction strengths between a pair of acetic acid molecules and between acetic acid-acetate anion are nearly iso-energetic. This finding confirms that the hydrogen bonded structure of liquid acetic acid is strongly modified upon dilution in the IL, even if such a “destruction” is only a metastable process.

Although the formation of acetic acid and carboxylate molecule in the CO₂-Bmim Ac mixture can now be taken for granted, we may question if the carboxylation reaction proceeds according to the two steps mechanism proposed in the literature. Indeed, in this scheme, it is the acid production that triggers the reaction by leading to the formation of a carbene species. The formation of acetic acid is considered as resulting from the interaction of the acetate anion with the Bmim cation independently of the presence of carbon dioxide. This assumption seems to be contradicted by the fact that the presence of acetic acid is only detected after the introduction of CO₂ in the IL and, therefore, appears as a consequence of the release of the proton after the carbene formation. Moreover, we do not detect the presence of acid in the pure ionic liquid either in our NMR measurements or in our Raman study.¹ As a consequence, the triggering of the reaction cannot be attributed to the formation of acetic acid. This finding reinforces two points. First, the relevance of the role played by CO₂ in triggering the reaction. Then, the dynamical aspect of the reactive process in the liquid phase through concerted mechanisms leading to the formation of “transient” CO₂-carbene complexes and acetic acid molecules as proposed in the reactive scheme discussed before. The two concerted mechanisms which are the chemical exchange of the acidic proton between the imidazolium ring and the acetate anion and the formation of a “transient” CO₂-1-butyl-3-methylimidazole-2-ylidene carbene complexes, respectively (step 1), can be viewed as a cooperative process taking place on a short time scale governed by the deprotonation of the C₂ site of the imidazolium cation interacting with acetate species. Indeed, the time scale of this latter elementary process (certainly in the subpicosecond range) avoids supposing the existence of long-lived carbene species formed in the mixture. Moreover, such a scenario is not unrealistic considering the order of magnitude of the values of the energy barriers of the isomerization process (step 1, 13.6 kcal/mol) and of the carboxylation reaction involving the transient CO₂ carbene species proposed here (step 2, 1.5 kcal/mol), which are likely significantly lowered in the dense phase due to the stabilization by the environment.¹

Influence of Water Traces on the Carboxylation Reaction. Ionic liquids are generally hygroscopic and the presence of water traces that possibly influence their thermodynamical and physical chemical properties is a matter of concern.^{24,36–38} This applies equally well for the CO₂-Bmim Ac system for which we may wonder if water traces have any influence on the carboxylation reaction, either as a catalyst

or in hampering the reaction by opening new byproduct pathways.⁵

In a series of experiments, we have considered the influence of water on the CO₂-Bmim Ac system. We have used dried Bmim Ac and prepared two mixtures containing 0.05 and 0.15 water molar fraction, respectively. The former concentration can be considered as the typical water content of undried IL, whereas the latter clearly corresponds to an unrealistic amount but it is aimed at magnifying any possible effect of water in the reactive processes occurring in the mixture. We have then introduced carbon dioxide in these mixtures under a pressure of 0.1 MPa, as described in the Experimental Section. The ¹³C NMR spectra of these two ternary mixtures are compared with the spectrum of the CO₂-Bmim Ac dried mixture in Figure 10.

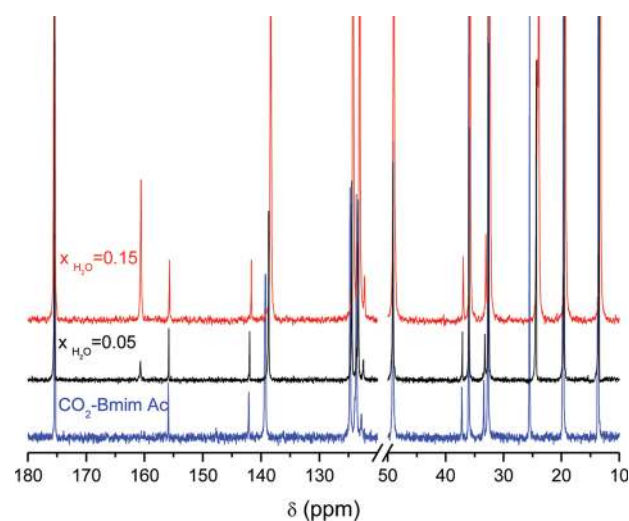


Figure 10. Influence of added water on the ¹³C NMR spectrum of the mixture CO₂-Bmim Ac.

It comes out that the presence of water, even at the higher concentration does not hamper the carboxylation reaction. This statement is supported by the observation of the resonance lines at about 155 ppm assigned to the carbon atom of CO₂ bonded to the C₂ atom of the imidazolium ring, as well as by the secondary resonance lines pertaining to the carboxylate species. We observe that the intensity of all the lines associated with the carboxylate species decrease as the water content increases in the mixture. In contrast, the extremely weak line at 160.2 ppm, which is barely observed in the binary mixture (with the dried Bmim Ac, Figure 3c) is clearly perceived in the 0.05 ternary mixture. The intensity of this line grows with the content of water and exceeds that of the line at about 155 ppm in the 0.15 mixture, showing that a new species which remains to be assigned is formed, whenever water is present in the mixture. We can also conclude that the presence of water traces leads to the formation of an additional adduct at the expense of the imidazolium carboxylate species. These results confirm also that the carboxylation reaction is not marginal even at unrealistic water contents.

Formation of New Adduct Due to Water Traces. We can be tempted to assign the new line at about 160 ppm to the formation of other carboxylate species, namely the 1-butyl-3-methylimidazolium-*n*-carboxylate with *n* = 4 and/or 5. Indeed, these compounds possess a resonance line at 163.09 ppm, a value close to that of the nonassigned new peak.¹⁸ However, as the reported chemical shifts of the resonance lines of carbons 4

and 5 for $n = 4$ and $n = 5$ are clearly different from the corresponding values reported for $n = 2$, we have established above that only the 1-butyl-3-methyl-imidazolium-2-carboxylate has been formed. Therefore, we can conclude that the line at about 160 ppm cannot be associated to a carboxylate species.

To assign the new line observed at about 160 ppm, we have performed measurements on an undried Bmim Ac–CO₂ mixture (water less than 0.05 mf) using labeled ¹³CO₂ to increase the intensity of the lines detected upon the introduction of carbon dioxide in the IL (Figure 11). As

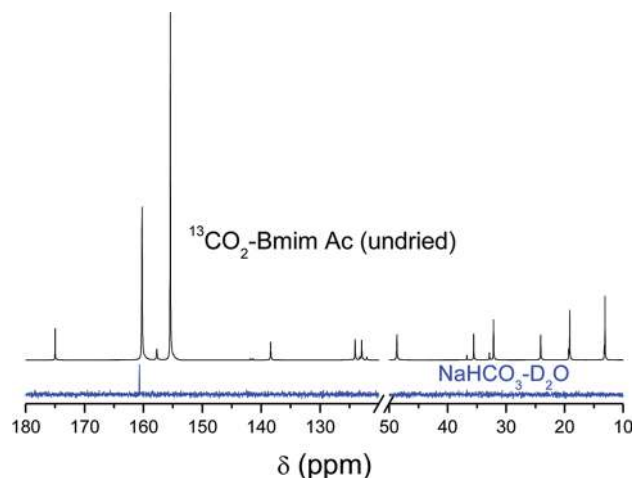


Figure 11. ¹³C NMR spectra of ¹³CO₂–Bmim Ac (undried) mixture and of a saturated solution of NaHCO₃ in D₂O.

expected, we notice that the lines at about 155 and 160 ppm are strongly enhanced compared to those of the ionic liquid. Moreover, we detect a new line at 157.7 ppm having an intensity of about 3% of the sum of the intensities of the other two lines and which was not obviously detected before using natural carbon dioxide.

This chemical shift domain is typical for formates, carboxylates, carbamates, carbonates, and hydrogen carbonates.^{39–44} On the basis of literature information, we have assigned the line at 160.2 ppm to the presence of a bicarbonate-like ion. To check this assignment, we have measured the ¹³C NMR spectrum of sodium bicarbonate (NaHCO₃) diluted at saturation in D₂O which confirms that a single resonance line is observed at 160.7 ppm (Figure 11).

At this level, it is noteworthy to note that the 2D INADEQUATE sequence shows that the extremely weak line at about 160 ppm, due to carbon atom of bicarbonate-like (HCO₃[−]) species is not correlated to the carbon atoms of the carboxylate molecule (either to the carbon atom of the COO or to the C2 atom) (Figure 6). This finding is a further proof of the formation of a different species from the carboxylate.

Influence of the Temperature on the CO₂–Bmim Ac Mixture. The ¹³C spectrum of ¹³CO₂–Bmim Ac has been measured in the temperature range 293–413 K with a 20 K step (Figure 12). Upon increasing the temperature, we observe that the position, intensity, and broadening (about 0.05 ppm close to the resolution) of the line at about 155 ppm remain almost unaffected up to 353 K. This line broadens and upfield shifts from 373 K, and in a 40 K variation, its width increases by a factor of about 25 (width about 1.3 ppm) in such a way that it becomes almost undetectable at 413 K. The line at about 160 ppm broadens continuously from room temperature to 333 K

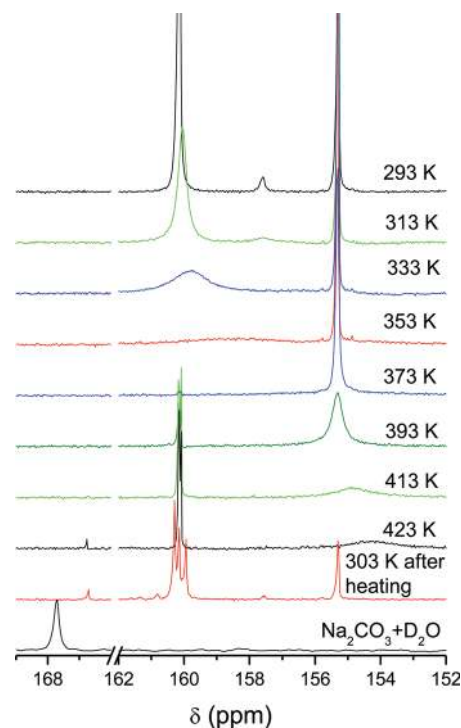


Figure 12. Temperature evolution of the proton decoupled ¹³C NMR spectra of ¹³CO₂–Bmim Ac (undried) in the region of the resonance lines of carbon dioxide, from 293 to 423 K, as well as at 303 K after heating. The spectrum of a saturated solution of Na₂CO₃ in D₂O is displayed for comparison.

(width varying from 0.1 ppm at room temperature to a value of about 1.3 ppm). Concomitantly, the weak line at about 158 ppm broadens to merge with the previous one at 333 K and a single line is observed that slightly shifts upfield. The resulting feature almost vanishes at 353 K and, for temperatures higher than 373 K, a doublet line is observed. Finally, at 423 K, the highest temperature investigated, a new line is detected at 167.2 ppm. After the temperature variation, the mixture ¹³CO₂–Bmim Ac has been allowed to cool and the spectrum measured at 303 K has been compared with the initial spectrum at room temperature (Figure 12). It appears that the intensities of the resonance lines of the sample before and after heating are comparable except for the two lines centered at about 155 and 160 ppm. Their intensity is reduced by at least 30% after the temperature cycling and the line at 160 ppm is no longer a single line. We also note that the new line detected at 167.2 ppm at 423 K is still present after cooling.

We have repeated these experiments on new samples but limiting the temperature variation to the range 293–353 K. We have observed that the evolution of the two resonance lines at 155 and 160 ppm was identical to the previous ones, showing the good reproducibility of our measurements. When the samples cooled to room temperature, we noticed that the spectra obtained before and after the temperature cycle were identical and therefore have not been affected by the temperature cycle. It is noteworthy that in the latest experiment, the line at 167.2 ppm is absent and a single line is observed at 160.2 ppm.

The difference between the temperature trends of the resonance line at about 155 ppm with the two others (160 and 158 ppm) can be understood by remembering that the former line is associated with the carbon atom of the carboxylate

moiety bonded to the imidazolium group. It has been shown above that the carboxylate molecule remains stable upon heating to temperatures ca. 413 K and becomes degraded by a further increase of the temperature (presence of the new line at 167.2 ppm).

It was shown that the decarboxylation temperature can be correlated with the frequency of the ν_{COO} asymmetric vibration and with the dihedral angle between the planes of the COO group and the imidazolium ring.¹⁹ The experimental value of the ν_{COO} asymmetric vibration and the calculated value for the dihedral angle that we obtained and reported in our Raman-DFT study allowed estimating that the decarboxylation temperature falls in the range 413–433 K.¹ These results allow inferring that the reduction of the intensity of the line at 155 ppm is correlated with a partial decarboxylation.

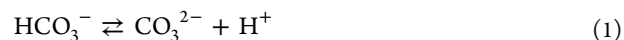
Therefore, we expect that the line remains first almost unaffected upon heating until some temperature value beyond which the line progressively vanishes, indicating that the compound becomes degraded. Indeed, the line at 155 ppm, almost unaffected up to 373 K, progressively vanishes up to 413 K. We note that the temperature range during which the degradation process is initiated and becomes effective is rather modest (about 40 K). The proof of the degradation of the carboxylate species is completed by considering the fact that cooling the sample to room temperature reduces the intensity of the 155 ppm line by about 30%. This shows that the carboxylate group of the 1-butyl-3-methylimidazolium-2-carboxylate to which this line is assigned has been partially removed from the ring during the temperature study. In addition, the concomitant observation of the new stable line at ca. 167.2 ppm should be correlated with this process. The value of this chemical shift suggests that a carbonate adduct has been formed in the course of the degradation. This assignment is supported by the ^{13}C NMR spectrum of sodium carbonate diluted at saturation in D_2O , which shows that the single resonance line of this compound is observed at 168.1 ppm (Figure 12), a value in good agreement with that reported above.

We may wonder if the partial decarboxylation of the imidazolium carboxylate could produce imidazolium–carbene or even imidazolium–carbene dimer. The existence of these species would lead to resonance lines situated at 210–220⁴⁵ and 124–130 ppm,^{46,47} respectively. We do not detect the weak resonance lines of these not ^{13}C labeled species at these chemical shifts. Therefore, in the absence of such signature we can discard the hypothesis of the existence of such species. We note that it was reported on a study about the reversible carboxylation of *N*-heterocyclic carbenes that the addition of $^{13}\text{CO}_2$ to the 1,3-diisopropyl-4,5-dimethylimidazol-2-carboxylate formed, directly by addition of CO_2 to the carbene or by deprotonation of the corresponding salt, led to an enhancement of the line assigned to the carbonyl group of the carboxylate.²³ This finding suggested to the authors that the bound CO_2 was equilibrating the free $^{13}\text{CO}_2$, which was confirmed by the attenuation of the signal with the reintroduction of CO_2 . Louie et al.²³ have also observed that in solution the carboxylate group could be exchanged between some imidazolylienes carboxylates and imidazolylienes leading to more stable imidazolylienes carboxylates. Although we deal with a different system we may also question if equilibrium occurs between the imidazolium carboxylate and their fragments, carbene and CO_2 . The existence of this equilibrium should lead to the appearance of the lines of the “free” CO_2 (at 125.4 ppm which is not

observed) and of the lines of an imidazolium carbene (not observed too, as referred before) under the hypothesis of a slow exchange, compared with the NMR time scale. The hypothesis of a very fast exchange does not appear probable taking into account the small value of the shift of the line at 155 ppm (about 1 ppm for 423 K). The broadening and shift of this line should be connected with the approach of the decarboxylation temperature (estimated to be in the range 413–433 K, as referred before). Therefore, under our experimental conditions such an equilibrium does not appear likely to occur and if it exists it is hard to put it in evidence taking also into account that CO_2 is involved in other reactions (formation of bicarbonate).

Considering now the resonance lines at 160 and 158 ppm, we noticed that these two lines are strongly affected by the temperature and almost vanish with a modest temperature increase (40 K). At last, considering the temperature evolution of the three lines, the difference between the broadening of the lines at 160 and 155 ppm and the fact that it is only at high temperature that a covalent bonding is expected to break, we may surmise that the species giving rise to the 160 and 158 ppm lines are certainly more labile and presumably involved in noncovalent type of interactions. This conclusion is consistent with the assignment to bicarbonate species proposed for the resonance line at 160 ppm.

Formation of Bicarbonate Species. We may now explain the origin of the resonance line observed at 160 ppm that we have assigned to a bicarbonate-like ion. For that purpose, we must recall that carbon dioxide in the presence of water produces carbonic acid (H_2CO_3), which in turn leads to the formation of hydrogen–carbonate ions (i.e., bicarbonate ions HCO_3^-). An acid–base equilibrium exists between bicarbonate ions with its conjugated base constituted by carbonate ions (CO_3^{2-}) according to the well-known chemical reaction



In ^{13}C NMR spectroscopy, because the interchange between these two species is fast on the observation time scale, only a sharp resonance is observed at a position corresponding to the concentration weighted average of the chemical shifts of the species in the absence of exchange, namely 169.4 and 161.4 ppm for the carbonate and bicarbonate ions, respectively.⁴⁸ Moreover, the equilibrium is pH dependent and is displaced in favor of the formation of bicarbonate species under acidic conditions. As a consequence, upon increasing the pH of the solution, the single resonance line shifts continuously between the values of the chemical shifts mentioned before (for the sites in the absence of chemical exchange) with typical values ranging from 162 ppm at pH \sim 6 to about 166 ppm at pH \sim 10.⁴⁹ On this ground, we may argue that the condition of observation of bicarbonate ions are gathered as we have traces of water and we also know that protons originating from the carboxylation reaction are present in large excess (compared to the water content), leading to the acetic acid formation. Indeed, the previous equilibrium must be displaced toward the bicarbonate formation. This conclusion allows interpreting both the presence of bicarbonate ions and the absence of the carbonate ions.

IV. CONCLUSION

As a final conclusion, we emphasize the richness of the solvation process of carbon dioxide in Bmim Ac, which appears

as a unique system that should deserve further consideration. The solvation process involves two distinct regimes as we pointed out before and which can be considered as a chemical and a physical regime, respectively. Our study agrees with the original proposition of Shiflett et al.⁵⁰ but, nevertheless, with marked differences concerning the nature of the processes involved in these regimes. Our results show that the chemical regime is not due to a chemical complexation in the sense of the formation of a reversible molecular complex between CO₂, as was proposed but corresponds to a true chemical reaction. Incidentally, it has been reported using electrochemistry techniques that the chemical absorption of CO₂ in Bmim Ac is not easily reversible.⁵¹

Several important issues have been covered here concerning the carboxylation reaction. The first one deals with the synthesis of the carboxylate itself. We found that this chemical can be obtained using simple and mild conditions consisting in a simple mixing of the reactants under very low pressure at room temperature. We found that the carboxylation reaction is highly selective and limited to the carboxylation of C₂ of the IL. This study has also allowed discussion of the chemical scheme proposed in the literature,²⁹ giving support not only to the existence of an irreversible carboxylation reaction taking place in the CO₂-Bmim Ac mixture but also to the predicted acetic acid formation that results from the introduction of the CO₂ in the IL. We have shown that nascent acetic acid molecules produced by the carboxylation reaction group interact with the acetate anion to form bidentate species. In these species, the COOH group of the acid interacts through a hydrogen bond with the available oxygen atom of the COO⁻ group of the nearby acetate anion, having the other oxygen atom hydrogen bonded to the imidazolium ring. These results support the indirect inference reached in our Raman study and confirmed by DFT calculations.¹ The long time evolution (40 day time period) of the CO₂-Bmim Ac mixture shows that the acid molecules tend to form again the cyclic dimers predominant in the pure acid.

Finally, we have discussed the first step of the carboxylation reaction as proposed in the literature on the ground of recent investigations on the Emim Ac.³⁰ We argued that this step is only valid in the vapor phase (at high temperature and very low pressure) in conditions very different from those involved in the liquid state. We came to the conclusion that the formation of carboxylate species, which is only observed after the introduction of carbon dioxide in the IL, could be possible if the CO₂ molecule interacts with the C₂ site during the time lapse in which the proton, exchanging between two sites, the Bmim Ac ion pair (I) and the N HC acetic acid complex (II), is preferentially located on site II. This led to a picture that demands consideration of the cooperativity of the processes between CO₂ and the moieties constituting the IL, as well as the time scale associated with the molecular interactions to explain the reaction triggering. Such a viewpoint, taking into account all the main features of chemical reactions in a dense phase, is more satisfying than a description of the elementary act of reaction as proposed in the literature which is only valid in the gas phase.

In the second part of this study, we have addressed the question of the influence of water traces, often present in "real" systems, on the carboxylation reaction. The presence of water leads to the formation of bicarbonate species at the expense of the carboxylate molecules. We have shown that even at unrealistic content (15% mf), water does not hamper the

carboxylation reaction to proceed, although a quite large amount of bicarbonate is formed.

In addition, a temperature study has shown that the carboxylate molecule is rather stable whereas the bicarbonate is more fragile. We also found that at high temperatures (433 K), these species are partially decomposed and that, after cooling at room temperature, they are again present in reduced proportion. Moreover, we detected that carbonate species is formed.

In spite of all the investigations that we have performed, we believe that a full understanding of the complete reactive scheme remains to be done, not only in the dried CO₂-Bmim Ac but also in the ionic liquid when water traces are present. In this context, kinetics studies appear important to shed light on the existence of a cooperative process taking place between carbon dioxide and the moieties constituting the IL to lead to the carboxylation, as we have suggested here.

We also believe that a close exploration of the possible chemical pathways, using the methods of quantum chemistry, would be an important step to perform investigation, in particular the question of the selectivity of the carboxylation reaction. In this context, we also surmise that these calculations should consider the influence of the supramolecular organization of the ionic liquid itself, which should play an important role. Indeed, in such highly organized complex liquids, it seems to us that an approach strictly limited to a few interacting species, although providing some clues, would possibly lead to an oversimplified picture of this remarkable system.

As a final comment, we note that the results presented here have also some incidence in the context of the solute recovery from ILs using supercritical CO₂ in the domain of the green chemistry.⁵² In this process, the ionic liquid is a priori supposed to not suffer degradation and could be recycled for further chemical operations. Clearly, the current study shows that this view should be taken with some caution for the present system, which would imply certainly further processing treatment, as pointed out by Barosse-Antle et al.⁵¹

■ ASSOCIATED CONTENT

📄 Supporting Information

¹H NMR spectra, ¹H-¹H COSY NMR spectra, and ¹H-¹³C HSQC and HMBC NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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