CO_2 Sequestration

DOI: 10.1002/anie.201305630

Solvation of Carbon Dioxide in $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$ Ionic Liquids Revealed by High-Pressure NMR Spectroscopy**

*Marta C. Corvo, João Sardinha, Sonia C. Menezes, Sandra Einloft, Marcus Seferin, Jairton Dupont, Teresa Casimiro, and Eurico J. Cabrita**

Dedicated to Professor Stefan Berger on the occasion of his retirement

Imidazolium-based ionic liquids (Im ILs) show relatively high CO_2 solubility and have been frequently investigated for CO_2 separation and absorption processes.[1] In most cases, Im ILs simply absorb the CO_2 physically, and the solubility is mainly controlled by the nature of the anion with the cation playing a minor role.[2] However, the optimal anion/cation combination or structural modification for tuning CO_2 solubility and selectivity requires a deeper understanding of the molecular details of CO_2 solvation. The rationalization of CO_2 solubility in Im ILs relies mainly in the combination of solubilization studies with molecular dynamics (MD) simulations,[3] but no doubt the importance of the theoretical approaches there is still a lack of experimental data aimed to directly probe specific CO_2-IL interactions, such as NMR or ATR-IR spectroscopy or X-ray diffraction, to complement the theoretical studies.[4] Herein we combine high-pressure (HP) NMR techniques with MD simulations to study the microscopic behavior of CO_2 dissolved in Im ILs in terms of solute–solvent interactions. Using 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate, ($[C_4mim]PF_6$ and $[C_4mim]BF_4$, respectively) we show that CO_2 solubility is essentially determined by the microscopic structure of the IL which is nanostructured in polar and nonpolar domains,[5] and we present a solvation model that integrates the most relevant previously reported theoretical and experimental data.

$^1H,^{19}F$ HOESY (heteronuclear Overhauser effect spectroscopy) experiments,[6] have been described as a method for the systematic study of the interactions between cations and anions in ILs, focusing on neat and conventional solvent mixtures.[7] We have used this approach to probe the cation–anion interactions in the absence and in the presence of CO_2 for two experimental p/T conditions (10 bar at 298 K and 80 bar at 313 K), corresponding to different molar fractions of dissolved CO_2 (0.17 and 0.14 at 10 bar/298 K for $[C_4mim]PF_6$ and $[C_4mim]BF_4$ respectively, and 0.41 for both ILs at 80 bar/313 K; see the Supporting Information for details about CO_2 quantification and full $^1H,^{19}F$ HOESY data). However, very recently a new model theory to analyze intermolecular NOEs in solution in general and in ILs was proposed by Gabl et al.[8] with implications for the previously accepted interpretations in terms of short-range effects ($d < 5$ Å). It was found that the experimental cross-relaxation rate give information on the mutual position of interacting species far beyond the first coordination shell rather than at the short distance range, with prevalence of long-range effects. In ILs, site-specific NOE may reflect the mean orientation of the ions over longer distances rather than the local structure of distinct ion aggregates. In this work, to account for the long range effects and avoid over interpretations in terms of local structure we focused on the changes in the NOE induced by the presence of CO_2 and combined the analysis of the NOE data with the results of MD simulations.

The $^1H,^{19}F$ HOESY results obtained for the pure ILs show a very similar cation–anion interaction pattern (Figure 1 a), with higher cross-peak intensities corresponding to higher relative cross-relaxation rates found between fluorine and the aromatic proton H2 followed by H4 and H5, which correspond to the preferential sites for cation–anion interaction.[7]

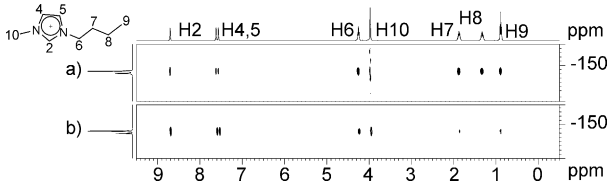

Figure 1. ^{19}F-HOESY spectra of a) neat $[C_4mim]BF_4$ at 313 K and b) mixed with 80 bar CO_2 at 298 K (600 ms mixing time).

[*] Prof. Dr. E. J. Cabrita
REQUIMTE-CQFB, Dep. Química, Fac. Ciências e Tecnologia
UNL, 2829-516 Caparica (Portugal)
E-mail: ejc@fct.unl.pt
Dr. M. C. Corvo, Dr. J. Sardinha, Dr. T. Casimiro
REQUIMTE-CQFB, Dep. Química, Fac. Ciências e Tecnologia
UNL, 2829-516 Caparica (Portugal)
Dr. S. C. Menezes
PETROBRAS/CENPES
21941-915 Rio de Janeiro, R.J. (Brazil)
Prof. Dr. S. Einloft, Prof. Dr. M. Seferin
PUCRS, Fac. Química
BR-90619900 Porto Alegre, RS (Brazil)
Prof. Dr. J. Dupont
Inst. Química-UFRGS
Av. Bento Gonçalves 9500, Porto Alegre (Brazil)

[**] This work was supported by Petróleo Brasileiro SA-PETROBRAS, Fundação para a Ciência e Tecnologia (FCT) and Ministério da Educação (CQFB Strategic Project PEst-C/EQB/LA0006/2011 and Project PTDC/QUI-QUI/098892/2008). The NMR spectrometers are part of the National NMR Network (RNRMN) and are funded by FCT (RECI/BBB-BQB/0230/2012).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201305630.

For the neat ILs at 298 K, the radial distribution functions (RDFs) and spatial distribution functions (SDFs) obtained from MD simulations for the anion around the cation are very similar (Supporting Information, Figure S2–S4). Both ILs show a preferential distribution of the anion around C2, C4 and C5 (Supporting Information, Figure S3) that goes beyond the first solvation shell as a result of their supramolecular organization.[9] Taking into consideration that the $^{1}H,^{19}F$ HOESY derived site specific cross-relaxations might be dominated by long-range effects, there is a good agreement between the experimental intermolecular NOE results and the MD simulation.

After CO_2 dissolution, the cation–anion contacts detected in the $^{1}H,^{19}F$ HOESY for both ILs are essentially the same as in the neat ILs. From the RDFs of the anion around the cation we observe that the CO_2 does not perturb the overall (short and long range) cation–anion orientation, in accordance with the NMR results (Supporting Information, Figure S5). The RDFs of the CO_2 molecule around the cation show that CO_2 is preferentially located toward the methyl group and the terminal CH_3 of the butyl group. This result is well demonstrated by a SDF (Supporting Information, Figure S6). However, in the $^{1}H,^{19}F$ HOESY the fluorine contacts with the nonpolar domain, specifically the methylene protons H6/7/8 and methyl group H9 are weaker. The effect is more clear at 80 bar (Figure 1 b), at which a higher molar fraction (0.41) of dissolved CO_2 is achieved. The NOE pattern suggests that the core of the polar domain maintains the same relative cation–anion orientation, but there are slight differences in the nonpolar domain.

It is well-accepted that Im ILs present a pre-organized 3D structure based in supramolecular aggregates mediated by hydrogen bonds and weak interactions.[5a,9] This organization creates a ion cage-like structure in the IL with void spaces, as was recently demonstrated in a number of Im ILs, including $[C_4mim]PF_6$ and $[C_4mim]BF_4$, by ^{129}Xe NMR.[10] The HOESY and MD data we have presented is consistent with CO_2 filling these void spaces with minimum changes of the ions self-organization. However, the HOESY data also indicate that increasing CO_2 pressure may lead to the deformation of the ion cage to accommodate more CO_2 molecules. Further NMR experiments in the presence of CO_2 were performed to clarify this idea.

Cation–cation interactions have been accessed with NOESY experiments, as described by Mele et al.[11] In a similar approach, we compared the map of homonuclear NOE cross-peaks in the presence and in the absence of CO_2 and analyzed the results having in mind the conclusions of Gabl et al.[8] as explained before. Cross-peaks between methyl group H10 and H7/8/9 of the aliphatic chain are particularly informative, as they reflect only intercationic interactions. Both neat ILs show this correlation at 298 K (Supporting Information, Figure S12) showing the IL charge order. However, comparing the NOESY data for neat IL with the CO_2-in-IL solutions, we conclude that CO_2 has an effect in the relative long-range cation–cation orientation in solution (Figure 2).

At 80 bar the pattern of cation–cation interactions changes considerably. Correlations between protons H10 and protons H7/8 are now almost absent from the spectra (Figure 2 a–c). In the MD simulations, subtle changes are also detected in the RDFs, the histograms for the C9–C10 distance (Figure 2 d) seem to indicate a reorganization of the butyl group upon addition of CO_2. In the case of $[C_4mim]PF_6$,

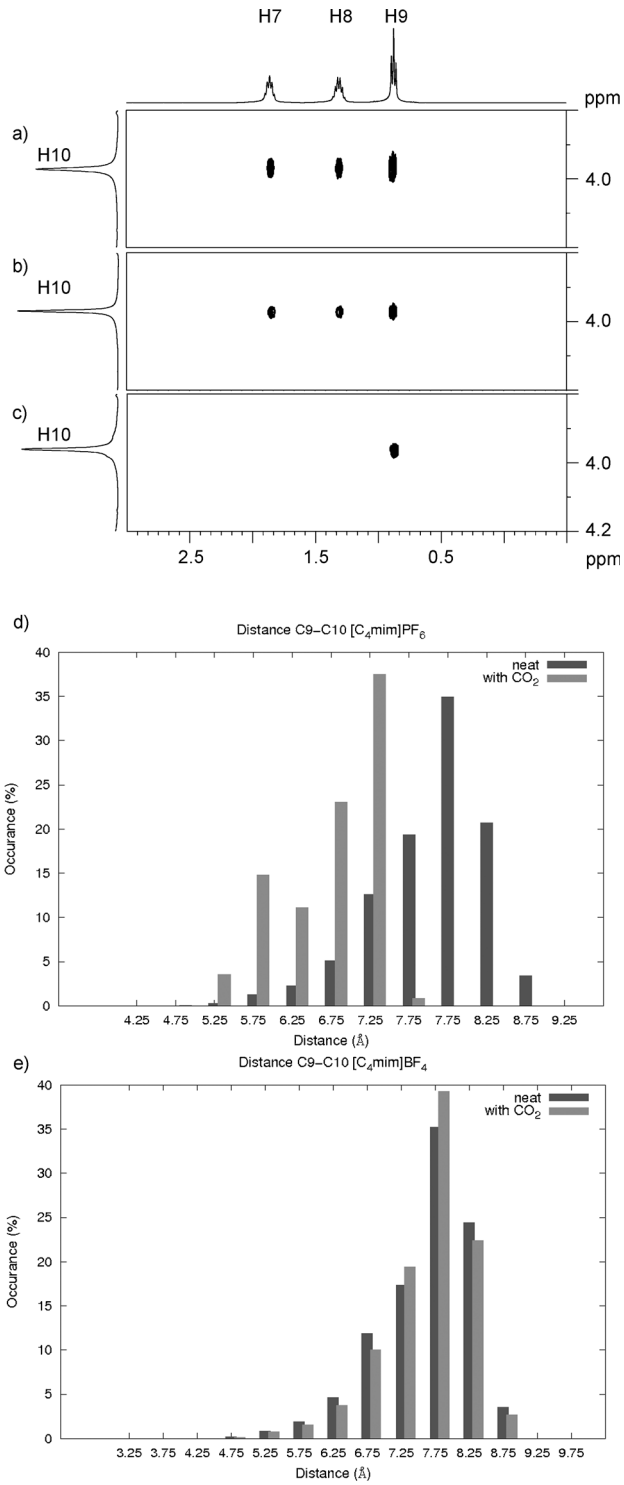

Figure 2. $^{1}H,^{1}H$ NOESY spectra (600 ms mixing time) of a) neat $[C_4mim]BF_4$ at 313 K, b) with CO_2, 10 bar, 298 K, and c) with CO_2, 80 bar, 313 K. d), e) Histograms with the C9–C10 distance in $[C_4mim]PF_6$ (d) and $[C_4mim]BF_4$ (e).

a dramatic decrease of this distance can be observed, which implies an approximation of the C terminal toward the Im ring. For $[C_4mim]BF_4$, this behavior is not so pronounced, which is probably due to the relative strength of the hydrogen-bonded Im aggregates of these two ILs. Indeed, it is well-known that the hydrogen bond between aggregates is stronger (almost 7 kcal mol^{-1}) in $[C_4mim]BF_4$ than in $[C_4mim]PF_6$. Therefore it is much easier to disrupt the supramolecular aggregates containing the PF_6 anion.[12] The experimental data indicates that besides void filling, to accommodate CO_2 different levels of adjustment of the pre-organized 3D structure of the IL might occur and that these are dependent of the anion type.

Information about the molecular reorientational dynamics of ILs can be obtained through ^{13}C NMR relaxation studies.[13] We determined the ^{13}C T_1 values for both ILs for all of the conditions under study (Supporting Information, Figure S16). Overall, the variations of the ^{13}C T_1 indicate that at low pressure (10 bar) the solubilization of CO_2 has a minimum effect in the global mobility of the IL but should be associated to a slight rearrangement of the orientation of the ions, leading to faster rotational motions of the C10 methyl carbon atom (see the Supporting Information for a more detailed analysis). At higher pressure and temperature CO_2 solubilization has a more pronounced effect in the global mobility, as the Im ring ^{13}C T_1 values are approximately three times larger than the ones determined for the neat IL at the same temperature. As in the low pressure case, the same effect in the T_1 of C10 is observed.

Taking into consideration all the experimental data presented, (HOESY, NOESY, and relaxation) and the MD results a possible preferential position for the CO_2 molecules can be inferred. This would be close to the anion, in the vicinity of methyl group 10, breaking the contact between cations and anions through the weaker cation–anion interactions but without changing significantly the stronger cation–anion contacts in the polar domain of the IL.

This data provides only an indirect indication of the relative position of CO_2. To probe direct cation–CO_2 and anion–CO_2 interactions, we performed $^{13}C,^{1}H$ HOESY and $^{13}C,^{19}F$ HOESY experiments for $[C_4mim]PF_6$ at 10 bar using ^{13}C-labeled CO_2 (Figure 3).

From the analysis of the cross-peaks from the $^{13}C,^{1}H$ HOESY experiments (Figure 3a) it can be seen that the interaction is stronger between CO_2 and the methyl protons H10, the aromatic protons H4/5 and methyl protons H9. The existence of direct anion-CO_2 interaction was also confirmed using $^{13}C,^{19}F$ HOESY (Figure 3c) and is in agreement with previous reported theoretical and experimental studies.[3b]

The MD simulations obtained for the ILs in the presence of CO_2 are in good agreement with the experimental data. In Figure 3b, the SDF for the anion and CO_2 near the cation show that CO_2 does not perturb the cation–anion interaction, and has a preferential location around H4/5 and H10. From the MD simulations it seems that the anion controls the location of CO_2, forcing it to reside near the Im ring, at the same time that the cation undergoes subtle changes to accommodate the gas molecules. A closer look at the cation interactions through the RDFs (Supporting Information,

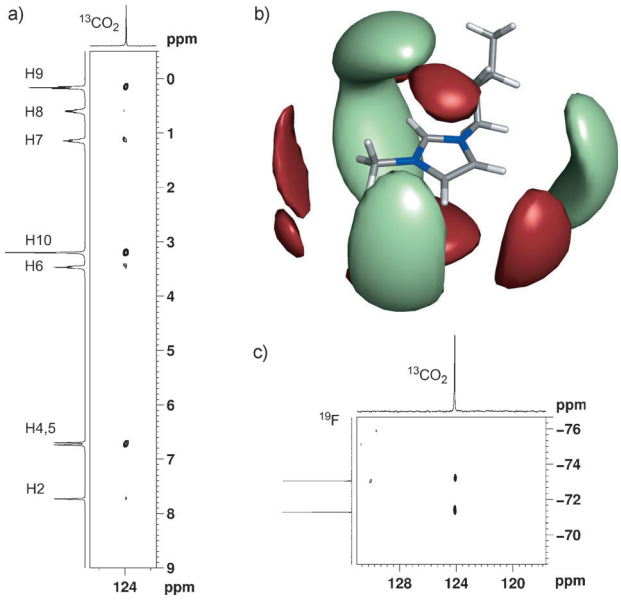

Figure 3. a) $^{13}C,^{1}H$ HOESY spectra (500 ms mixing time); b) SDF for the PF_6^- (green) and CO_2 (red) near the $[C_4mim]^+$ cation; c) $^{13}C,^{19}F$-HOESY (400 ms mixing time) of $[C_4mim]PF_6$ mixed with $^{13}CO_2$, 298 K, 11 bar.

Figure S6) confirms that CO_2 prefers to reside near the methyl groups. The strong C9–CO_2 interaction can be ascribed to the flexibility of the butyl group in which the terminal carbon is closer to the Im ring in the ILs/CO_2 mixtures. To our knowledge, this is the first unequivocal experimental evidence of a preferential CO_2 distribution towards the cation. Interestingly, the RDF of the PF_6/BF_4 and CO_2 around the C2 carbon of the Im, shows that the second solvation shell of the CO_2 is located between the first and the second shell of the anions, confirming that CO_2 does not interfere substantially in the short range cation–anion orientation, and is located preferentially in the voids in the IL network. A similar result was found for the solubilization of CO_2 in $[C_4mim]$TFA using a combination of Raman spectroscopy and ab initio calculations.[4d]

In conclusion, although there seems to be a consensus regarding the proximity of CO_2 near the anion as was shown by ATR-IR study of CO_2 expanded-ILs[14] and which we have also observed by NMR, the location near the cation is more ambiguous. Both our experimental and our simulation results reinforced the idea that the behavior of CO_2 towards the cation has been poorly understood. Even at low molar fractions, our results are in accordance with CO_2 residing in cavities near methyl groups H9 and H10, and aromatic protons H4,5. This is in contrast with the possible competition between CO_2 and the anion above and below the Im ring[3b] and the formation of hydrogen bonds between CO_2 and the H2 of Im ring as recently reported.[15] CO_2 is not competing with the anion for the same locations in relation to the cation as it is establishing weaker interactions. The preferential site for CO_2 location near methyl groups is possibly explained with the existence of local conformational equilibrium and consequent greater probability of cavity formation. A significant cation effect in CO_2 solvation in chemical absorbing

1,3-dialkylimidazolium acetates ILs was recently highlighted by Kirchner[16a] based in a number of previously reported experimental observations,[16b–f] herein we extend the cation intervention to other ILs not engaged in chemical absorption. The IL structure suffers only subtle changes with CO_2 solvation without disrupting the cation–anion hydrogen bonds, suggesting that this may be the main factor controlling CO_2 solubilization. This knowledge of the molecular details of CO_2 solvation is crucial not only for the design of better ILs for CO_2 capture but for the development of tailor-made IL sensor and separation devices.

Received: July 1, 2013
Revised: August 21, 2013
Published online: October 9, 2013

Keywords: CO_2 sequestration · ionic liquids · molecular dynamics · NMR spectroscopy

[1] a) X. Zhang, X. Zhang, H. Dong, Z. Zhao, S. Zhang, Y. Huang, *Energy Environ. Sci.* **2012**, *5*, 6668–6681; b) J. F. Brennecke, B. E. Gurkan, *J. Phys. Chem. Lett.* **2010**, *1*, 3459–3464.
[2] a) J. E. Bara, T. K. Carlisle, C. J. Gabriel, D. Camper, A. Finotello, D. L. Gin, R. D. Noble, *Ind. Eng. Chem. Res.* **2009**, *48*, 2739–2751; b) M. Hasib-ur-Rahman, M. Siaj, F. Larachi, *Chem. Eng. Process.* **2010**, *49*, 313–322; c) M. Ramdin, T. W. de Loos, T. J. H. Vlugt, *Ind. Eng. Chem. Res.* **2012**, *51*, 8149–8177.
[3] a) C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke, E. J. Maginn, *J. Am. Chem. Soc.* **2004**, *126*, 5300–5308; b) X. Huang, C. Margulis, *J. Am. Chem. Soc.* **2005**, *127*, 17842–17851.
[4] a) Y.-F. Hu, Z.-C. Liu, C.-M. Xu, X.-M. Zhang, *Chem. Soc. Rev.* **2011**, *40*, 3802–3823; b) S. G. Kazarian, B. J. Briscoe, T. Welton, *Chem. Commun.* **2000**, 2047–2048; c) M. Kanakubo, T. Umecky, Y. Hiejima, T. Aizawa, H. Nanjo, Y. Kameda, *J. Phys. Chem. B* **2005**, *109*, 13847–13850; d) M. I. Cabaço, M. Besnard, Y. Danten, J. A. Coutinho, *J. Phys. Chem. B* **2011**, *115*, 3538–3550.
[5] a) J. Dupont, *J. Braz. Chem. Soc.* **2004**, *15*, 341–350; b) J. N. A. Canongia Lopes, A. A. H. Pádua, *J. Phys. Chem. B* **2006**, *110*, 3330–3335.
[6] A. Mele, C. D. Tran, S. H. De Paoli Lacerda, *Angew. Chem.* **2003**, *115*, 4500–4502; *Angew. Chem. Int. Ed.* **2003**, *42*, 4364–4366.
[7] Y. Lingscheid, S. Arenz, R. Giernoth, *ChemPhysChem* **2012**, *13*, 261–266.
[8] S. Gabl, O. Steinhauser, H. Weingartner, *Angew. Chem.* **2013**, *125*, 9412–9416; *Angew. Chem. Int. Ed.* **2013**, *52*, 9242–9246.
[9] J. Dupont, *Acc. Chem. Res.* **2011**, *44*, 1223–1231.
[10] F. Castiglione, R. Simonutti, M. Mauri, A. Mele, *J. Phys. Chem. Lett.* **2013**, *4*, 1608–1612.
[11] A. Mele, G. Romanò, M. Giannone, E. Ragg, G. Fronza, G. Raos, V. Marcon, *Angew. Chem.* **2006**, *118*, 1141–1144; *Angew. Chem. Int. Ed.* **2006**, *45*, 1123–1126.
[12] F. C. Gozzo, L. S. Santos, R. Augusti, C. S. Consorti, J. Dupont, M. N. Eberlin, *Chem. Eur. J.* **2004**, *10*, 6187–6193.
[13] M. Imanari, K.-I. Uchida, K. Miyano, H. Seki, K. Nishikawa, *Phys. Chem. Chem. Phys.* **2010**, *12*, 2959–2967.
[14] T. Seki, J.-D. Grunwaldt, A. Baiker, *J. Phys. Chem. B* **2009**, *113*, 114–122.
[15] K. Dong, S. Zhang, *Chem. Eur. J.* **2012**, *18*, 2748–2761.
[16] a) O. Hollóczki, Z. Kelemen, L. Könczöl, D. Szieberth, L. Nyulászi, A. Stark, B. Kirchner, *ChemPhysChem* **2013**, *14*, 315–320; b) G. Gurau, H. Rodríguez, S. P. Kelley, P. Janiczek, R. S. Kalb, R. D. Rogers, *Angew. Chem.* **2011**, *123*, 12230–12232; *Angew. Chem. Int. Ed.* **2011**, *50*, 12024–12026; c) M. I. Cabaço, M. Besnard, Y. Danten, J. A. P. Coutinho, *J. Phys. Chem. A* **2012**, *116*, 1605–1620; d) M. Besnard, M. I. Cabaco, F. V. Chávez, N. Pinaud, P. J. Sebastiao, J. A. P. Coutinho, J. Mascetti, Y. Danten, *J. Phys. Chem. A* **2012**, *116*, 4890–4901; e) M. Besnard, M. I. Cabaco, F. V. Chávez, N. Pinaud, P. J. Sebastiao, J. A. P. Coutinho, Y. Danten, *Chem. Commun.* **2012**, *48*, 1245–1247; f) M. B. Shiflett, B. A. Elliott, S. R. Lustig, S. Sabesan, M. S. Kelkar, A. Yokozeki, *ChemPhysChem* **2012**, *13*, 1806–1817.

