

Studying the Solubility of CO₂ in Ionic Liquids Using High Pressure NMR

Marta Corvo,^{1*} Sonia Cabral de Menezes,² Tatiana O. Magalhães,³ Marcus Seferin,³ Sandra Einloft,³ Teresa Casimiro,¹ Eurico J. Cabrita¹

[1] REQUIMTE,CQFB, Dept. Química, Faculdade de Ciências e Tecnologia, Univ. Nova Lisboa, 2829-516 Caparica, Portugal

[2] PETROBRAS/CENPES, 21941-915 Rio de Janeiro, R.J., Brazil

[3] Pontifícia Univ. Católica Rio Grande do Sul, Fac. Química, BR-90619900 Porto Alegre, RS Brazil

marta.corvo@dq.fct.unl.pt

INTRODUCTION

Global warming has prompted the scientific community to look for new strategies for CO₂ capture and storage. The reduction of greenhouse gas emissions is a demanding task in the climate change mitigation efforts.[1] The existing technology for CO₂ capture is dominated by amine-based processes, where CO₂ reacts with alkanolamines forming carbamate/carbonate in aqueous solutions. These amine solutions present some disadvantages such as the loss solvent through evaporation, formation of corrosive byproducts, and high energy consumption during regeneration.[2] Recent studies suggest that ionic liquids (ILs) can be an alternative material for CO₂ capture due their high selectivity for CO₂ absorption. [1,3]. ILs physical and chemical properties can be enhanced and modified by both their cationic and anionic moieties, which has prompted them a broad range of applications. Therefore, considering that ILs properties can be tailor-designed to satisfy the specific application requirements, the use of ILs for CO₂ capture has received a considerable interest in the last years.

Imidazolium ILs are one of the most explored ILs families. Experimental and simulation studies have shown that alkylimidazolium ILs have the highest CO₂ solubilities. The anion moiety is believed to have the strongest influence in the solvation process.[4]

In an effort to contribute to the understanding of CO₂-philicity, herein we present a detailed analysis of the results obtained for ILs with different solvation capabilities - BMIMPF₆, BMIMNTf₂ and BMIMBF₄. Using High Pressure NMR (HP-NMR) we were able to determine the CO₂ molar fraction in these ILs, obtaining results that are in good agreement with the reported solubility.[5,6] Nuclear Overhauser Effect based experiments were used to determine relative cation/anion orientations in the IL before and after CO₂ absorption. Multinuclear diffusion NMR experiments, using the pulsed gradient spin echo (PGSE) techniques, allowed a relative quantification of the strength of the ion pair interaction for different combinations of cation/anion.

This methodology gives an insight to the nature of cation/anion/CO₂ relationship, establishing a procedure for a molecular based interpretation for the solvation mechanisms. The disclosed molecular interactions between CO₂ and the ILs enable the rationalization of the underlying characteristics for developing better solvents for CO₂.

To develop an understanding of the real potential of ILs as an effective media for CO₂ capture, we aimed at developing a High Pressure NMR based methodology for measuring not only CO₂ solubility in ionic liquids, but also the strength of the interactions between CO₂ and ILs.

MATERIALS AND METHODS

BMIMPF₆, BMIMNTf₂ and BMIMBF₄ were purchased from SOLCHEMAR, Lda. (>98% purity). All ionic liquids were dried under vacuum at 40°C for 24 hours before used. Carbon dioxide was supplied by Air Liquide with purity better than 99.998%.

The medium pressure NMR experiments were conducted in a Wilmad-Glass tube. The HP-NMR experiments were conducted in a 5 mm sapphire tube with a titanium valve purchased from SUN NANOTECH.

All NMR spectra were acquired in a Bruker Avance III 400 spectrometer equipped with a temperature control unit, and a pulse gradient unit capable of producing magnetic field pulsed gradients in the z-direction of 56.0 G/cm, operating at 400.15 MHz for hydrogen, 100.61 MHz for carbon and 376.90 MHz for fluorine.

In a typical HP-NMR experiment 0.3 ml of IL was loaded directly inside the NMR tube and the system was placed under vacuum in a thermostated water bath at the desired temperature. The HP-NMR tube was then pressurized up to desired pressure with CO₂, (using a HIP manual compressor for the experiments at 80 bar). The system was considered to have reached equilibrium if the pressure of the system had been unchanged with time for 12 h. The tube was then transferred to the NMR apparatus using a protective polycarbonate structure.

NMR experiments: ¹³C NMR inverse gated ¹H decoupled spectra were obtained with a relaxation delay between 30 and 60 seconds, according to the CO₂ T1. Typically, in each experiment 128 transients with 64K data points were collected, corresponding to an average duration of 1-2 h. ¹³C T1 measurements were performed using an inversion recovery experiment.

¹³C diffusion measurements were performed using a stimulated echo sequence using bipolar sine gradient pulses and eddy current delay before the detection with proton broadband decoupling during acquisition.[7] The signal attenuation is given by:

$$S = S_0 \exp\left(-\gamma^2 g^2 D \delta^2 \left(\Delta - \frac{2\delta}{3} - \frac{\tau_g}{2}\right)\right)$$

where D denotes the self-diffusion coefficient, γ the gyromagnetic ratio, δ the gradient pulse width, Δ the diffusion time, τ_g the gradient recovery delay and g the gradient strength corrected according to the shape of the gradient pulse.

Typically, in each experiment a number of 16 spectra of 64K data points were collected, with values for the duration of the magnetic field pulse gradients (δ) of 3 to 6 ms, diffusion times (Δ) of 400 to 800 ms, and an eddy current delay set to 5 ms. The pulse gradient (g) was incremented from 5 to 95% of the maximum gradient strength in a linear ramp.

¹H, ¹⁹F – HOESY experiments were acquired using a phase sensitive pulse sequence with a mixing time between 50 to 1500 ms. 16 transients were collected with a spectral width of *ca* 5000 Hz in $F2$ (¹H) and 2000 Hz in $F1$ (¹⁹F), in a total of 2K data points in $F2$ and 128 data points in $F1$, the relaxation delay was set to 2.0 s.

RESULTS

CO₂ solubility measurements

CO₂ solubility measurements reported in literature involve frequently gravimetric or stoichiometric methods, or the use of techniques like ATR-IR or X-ray diffraction.[8] In this

work we have validated an alternative methodology based in ^{13}C NMR spectroscopy that allows the measurement of the CO_2 mole fraction directly from the IL/ CO_2 solution (Fig. 1). Routine ^{13}C NMR spectra are normally acquired under conditions that do not allow quantification, however, quantitative ^{13}C NMR spectra can be obtained using the inverse gated ^1H decoupled experiment with a correct relaxation delay that ensures full relaxation of the ^{13}C nuclei.

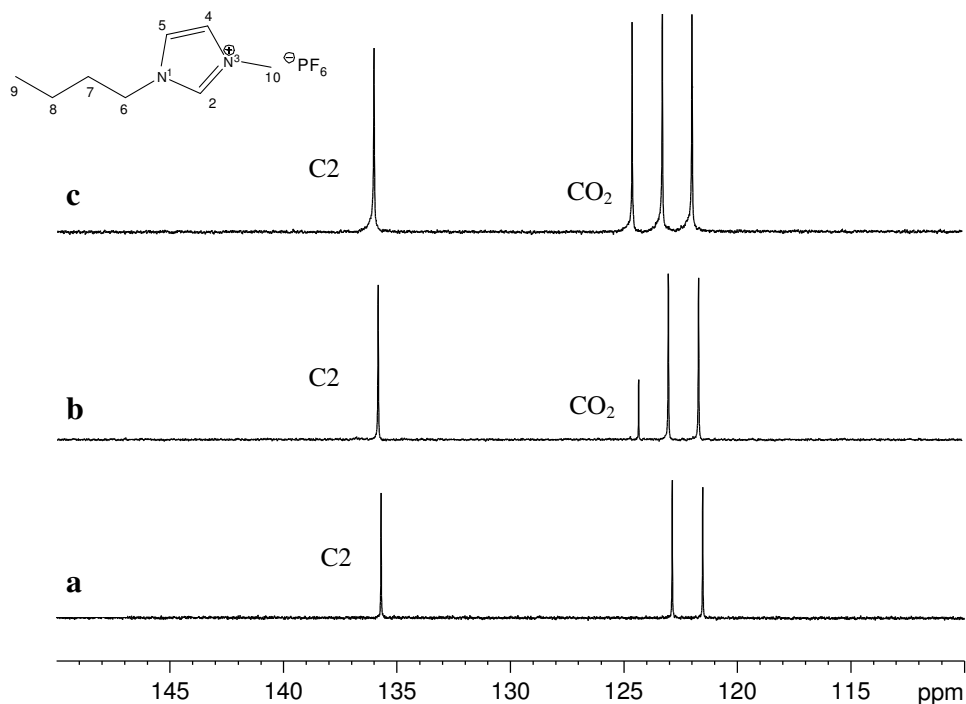


Figure 1 : Expansion of the ^{13}C NMR spectra of BMIPF_6 : a) ^1H decoupled spectra of pure IL, 298K; b) inverse gated ^{-1}H decoupled spectra of $\text{IL}+\text{CO}_2$, 10bar and 298K; c) inverse gated ^{-1}H decoupled spectra of $\text{IL}+\text{CO}_2$, 80bar and 313K.

CO_2 quantification was achieved using the ratio of the integrals of the CO_2 resonance signal and the C2 carbon from the imidazolium ring. CO_2 molar fractions, for the studied ILs and under different conditions are shown in Table 1. The results are in good agreement with previously reported values.

Table 1 : CO_2 molar fractions determined by ^{13}C NMR.

IL	X_{CO_2}	lit	X_{CO_2}	lit
	298K, 10 bar CO_2		313K, 80 bar CO_2	
BMIMPF_6	0.17	0.16 ^[9]	0.41	0.41 ^[5]
BMIMBF_4	0.14	0.15 ^[9]	0.41	0.42 ^[10]
BMIMNTf_2	0.33	0.24 ^[9]	0.62	0.71 ^[5]

CO₂ diffusion

Knowledge of the diffusivity behaviour of gases in ILs is important for the design and development of IL based processes. We have measured the CO₂ self-diffusion coefficient (D) in the three ILs by means of the ¹³C detected PGSE NMR technique at two different pressures (10 and 80 bar, Table 2). In order to evaluate the possibility of errors in the diffusion coefficients due to convection arising from temperature gradients forming along the NMR tube axis, experiments using the double stimulated echo for convection compensation were also performed, but the results were identical.[11,12]

Table 2 : CO₂ diffusion coefficients.

IL	D _{CO2} (m ² s ⁻¹) 298K, 10 bar CO ₂	Viscosity 298K pure IL[13]	D _{CO2} (m ² s ⁻¹) 313K, 80 bar CO ₂	Viscosity 313K pure IL[13]
BMIMPF ₆	2.44E-10	249.6	9.14E-10	106.1
BMIMBF ₄	6.97E-11	99.6	8.08E-10	47.4
BMIMNTf ₂	1.11E-10	49.9	4.57E-10	27.5

Interestingly, BMIMPF₆ is the IL where CO₂ presents the higher diffusion coefficient. This is the more viscous IL in the series [13]. This seems to indicate that the liquid structure of this IL is more perturbed by the CO₂ dissolution than the other two and points to a dramatic change in its viscosity due to CO₂ dissolution. This effect is best seen by comparing BMIMNTf₂ and BMIMPF₆; BMIMNTf₂ is much less viscous than BMIMPF₆ and the molar fraction of dissolved CO₂ in this IL is almost the double of that of BMIMPF₆, even so the diffusion coefficient of CO₂ in BMIMPF₆ is always higher than in BMIMNTf₂.

Anion/cation interaction

The cation/anion interactions can be probed by NMR spectroscopy through intermolecular nuclear Overhauser enhancements (NOEs).[14] In fluorine containing ILs it's possible to gain insight into the short-range structure by heteronuclear ¹H, ¹⁹F- NOEs experiments (¹H, ¹⁹F – HOESY). HP-NMR enables the study of the effects of CO₂ solvation in ILs, by probing the cation/anion interaction. Figure 2 shows ¹H, ¹⁹F–HOESY spectra for the pure IL and mixed with CO₂ at 80 bar (X_{CO2}=0.41), both at 313K. The changes in the intensity of the correlations found in both spectra are indicative of changes in the IL structure.

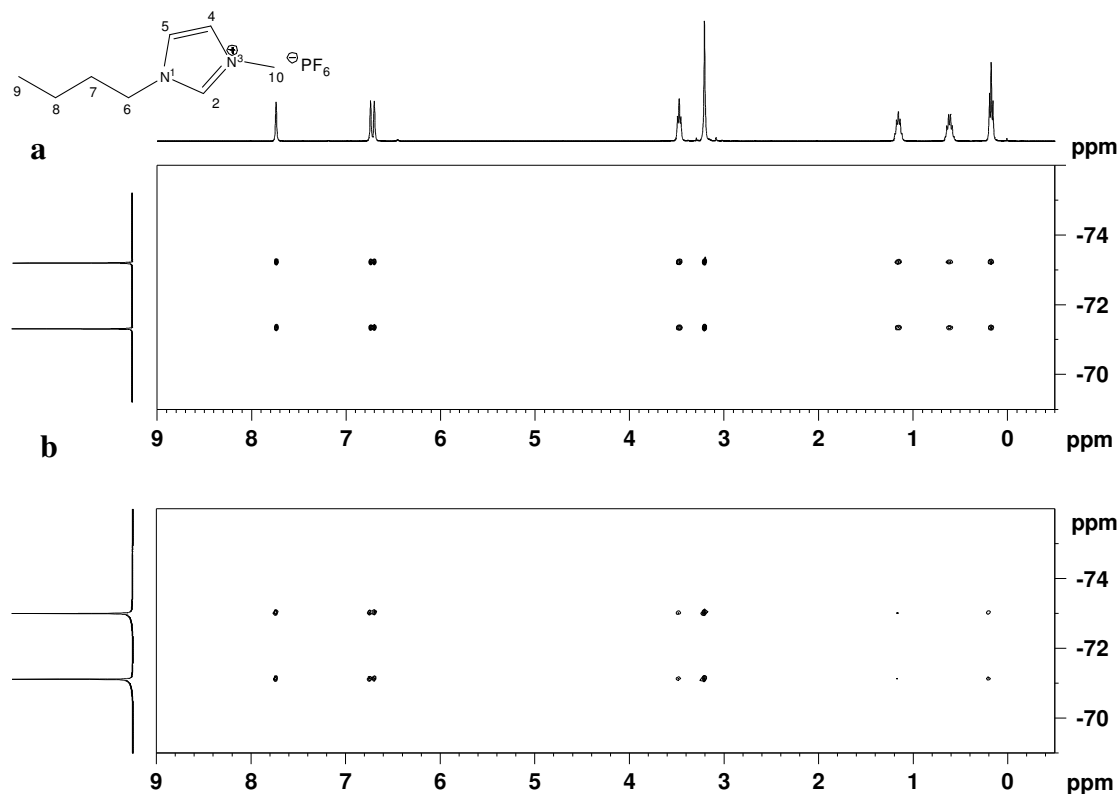


Figure 2 : ¹H, ¹⁹F – HOESY spectra of BMIMPF₆ at 313K (600ms mixing time) – pure IL (a) and IL /CO₂, 80bar (b).

Careful analysis of the ¹H – ¹⁹F correlations and relative intensities allows to determine preferential interaction regions between cation and anion. Higher intensities are found in the pure IL for the aromatic imidazolium protons H2 followed by H4 and H5, which correspond to the preferential regions for cation/anion interaction, however all protons show correlations with fluorine. After CO₂ dissolution all interactions are weaker, depicting a dilution effect caused by CO₂ and showing that the ion pair was perturbed. This effect was detected for the three ILs but is more significant in BMIMPF₆, in agreement with the diffusion results discussed previously.

CONCLUSION

HP-NMR is a powerful technique that enables the study of IL/CO₂ mixtures, allowing solubility measurements in a simple and direct way, as well as the analysis of the effects of CO₂ solvation in ILs, by probing the cation/anion interaction and CO₂ diffusion coefficients. Solubility measurements obtained through this methodology are in good agreement with previously reported values.

AKNOWLEDGMENTS

The authors would like to thank Petróleo Brasileiro SA - PETROBRAS and Fundação para a Ciência e Tecnologia (Project PTDC/QUI-QUI/098892/2008) for financial support, and Graciane Marin (UFRGS) for providing the ionic liquids. The NMR spectrometers are part of the National NMR Network (RNRMN) and are funded by Fundação para a Ciência e a Tecnologia.

REFERENCES :

- [1] D'ALESSANDRO, D. M.; SMIT, B.; LONG, J. R. *Angew. Chem. Int. Ed.*, Vol. 49, **2010**, p. 6058.
- [2] KARADAS, F. ; ATILHAN, M.; APARICIO, S. *Energy Fuels*, Vol. 24, **2010**, p. 5817.
- [3] ANTHONY, J. L.; MAGINN, E. J.; BRENNECKE, J. F. *J. Phys. Chem. B*, Vol. 106, **2002**, p. 7315.
- [4] HASIB-UR-RAHMAN, M.; SIAJ, M. ; LARACHI, F. *Chem. Eng. and Process.*, Vol. 49, **2010**, p. 313.
- [5] AKI, S. N. V.K.; MELLEIN, B. R.; SAURER, E.M.; BRENNECKE, J.F. *J. Phys. Chem. B*, Vol. 108, **2004**, p. 20355.
- [6] ANDERSON, J. L.; DIXON, J. K.; BRENNECKE, J.F. *Acc. Chem. Res.*, Vol. 40, **2007**, p. 1208.
- [7] WU, D.; CHE, A.; JOHNSON, C. S. JR., *J. Magn. Reson.*, Vol. A115, **1995**, p. 260.
- [8] YU-FENG HU, ZHI-CHANG LIU, CHUN-MING XU AND XIAN-MING ZHANG *Chem. Soc. Rev.*, Vol. 40, **2011**, p. 3802.
- [9] ANTHONY, J.L.; ANDERSON, J.L.; MAGINN, E.J. ; BRENNECKE, J.F. *J. Phys. Chem. B*, Vol. 109, **2005**, p. 6366.
- [10] YUHUAN, C.; SUOJIANG Z. ; XIAOLIANG Y. ; YANQIANG, Z.; XIANGPING, Z.; WENBIN, D.; RYOHEI, M. *Thermochimica Acta*, Vol.441, **2006**, p. 42.
- [11] PELTA, D. ; BARJAT, H.; MORRIS, G.A. ; DAVIS A.L. ; HAMMOND, S.J. *Magn. Reson. Chem.*, Vol. 36, **1998**, p.706.
- [12] JERSCHOW, J.; MÜLLER, N. *J. Magn. Reson.*, Vol. 125, **1997**, p.372.
- [13] TOKUDA, H.; TSUZUKI, S.; SUSAN, MD.; HAYAMIZU, K.; WATANABE, M. *J. Phys. Chem. B*, Vol. 110, **2006**, p. 19593.
- [14] MELE, A.; TRAN, C.D.; LACERDA, S. H. P. *Angew. Chem. Int. Ed.* Vol. 42, **2003**, p. 4364.