# Diffusion and Chemical Exchange in Mixtures of Carbon Dioxide and an Amine-Functionalized Ionic Liquid by High Field NMR

E. Hazelbaker (U. of Florida, Chem. Eng.); E.J. Maginn(U. of Notre Dame, Chem. Biomol. Eng.); J.K. Shah (U. of Notre Dame, Chem. Biomol. Eng.); S. Vasenkov (U. of Florida, Chem. Eng.)

## Introduction

Development of highly efficient absorbents for the removal of carbon dioxide from power plant emissions and gas mixtures containing energy carriers, such as flue gas and natural gas, becomes an increasingly urgent task. While processes based on $CO_2$ capture by aqueous amine solutions found applications in natural gas sweetening, it is realized that replacement of these solvents by other types of liquid absorbents that are more stable and require less energy for carbon dioxide desorption would be extremely desirable. Ionic liquids, molten salts that are liquid at temperatures around room temperature, represent a promising class of such absorbents.

This work concerns NMR studies of the mixture of $CO_2$ and a task-specific ionic liquid (TSIL). The main focus of these studies was on the investigation of the relationship between $CO_2$ diffusion and chemical exchange of $CO_2$ in the mixture, i.e. the process of $CO_2$ exchange between the chemically-bound (chemisorbed) and physisorbed states in the mixture of $CO_2$ and the TSIL.

## Experimental

The TSIL chosen for the studies is composed of $(CH_3)_3N(CH_2)_2NH_2^+$ cation and $(CF_3SO_2)_2N^-$ anion. Diffusion data were obtained by C-13 pulsed field gradient (PFG) NMR using a wide-bore 17.6 T Bruker BioSpin spectrometer located at AMRIS, University of Florida. Magnetic field gradients with the amplitude up to 30 T/m were generated using diff60 diffusion probe and Great60 gradient amplifier (Bruker BioSpin). The same wide-bore 17.6 T Bruker BioSpin spectrometer was employed to carry out C-13 NMR exchange experiments (EXSY) to investigate an exchange of $CO_2$ between the chemisorbed and physisorbed states. One-dimensional (1D) EXSY sequence [(selective π/2) - π/2 - $\tau_{mix}$ - π/2 – Acquisition] with a selective excitation pulse was used.

## Results and Discussion

$^{13}C$ 1D EXSY measurement allowed obtaining the residence times of $CO_2$ in the chemisorbed and physisorbed states.[1] These residence times were found to be, respectively, 76 and 8.8 ms. $^{13}C$ PFG NMR diffusion measurements of the ions and $CO_2$ were performed using the standard stimulated echo PFG NMR sequence for the effective diffusion times comparable with and much larger than the values of the mean residence times of $CO_2$ reported above (Fig.1). "Chemisorbed $CO_2$" and "Physisorbed $CO_2$" in Fig. 1 indicate ensembles of $CO_2$ molecules that were, respectively, in the chemisorbed and physisorbed states during acquisition time interval of the PFG NMR sequence and can be in any state during the remaining part of the diffusion time. It is seen in Fig.1 that the diffusivities of the two $CO_2$ ensembles are different at short diffusion times, but approach the same diffusivity with increasing diffusion time.[1] The ion diffusivities do not show any dependence on diffusion time.

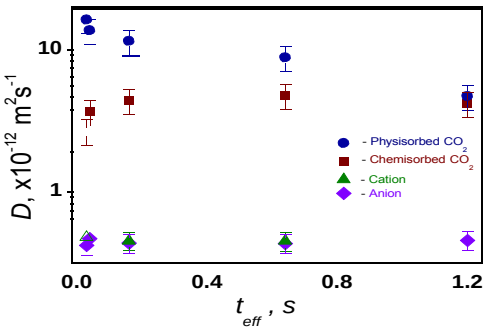


**Fig. 1.** Dependence of the apparent diffusivities of different types of species in the mixture of $CO_2$ and the TSIL on diffusion time.

## Conclusions

High field NMR was used to study interplay of diffusion and chemical exchange in mixtures of TSIL and $CO_2$.

## Acknowledgements

We are grateful for the financial support of this work by NSF (CBET No. 0967703) and by the external user program of the NHMFL (project No. P01953 and P07167).

## References

[1] Hazelbaker, E. *et al*., 2013 AIChE Annual Meeting, San Francisco, CA, # 330204 (2013).