Exchange Kinetics of CO_2 Molecules between the Reacted and Unreacted States in the Mixtures of an Ionic Liquid and CO_2 by High Field NMR

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Introduction

Ionic liquids (ILs) are molten salts that are liquid at temperatures around room temperature. ILs represent a promising class of absorbents for replacing traditional aqueous amine solvents in carbon dioxide capture. They can be tailored to exhibit a number of useful properties including negligible vapor pressure and high thermal stability. It has been demonstrated that chemical modification of an ionic liquid by covalent tethering of an amine group to the cation results in a highly selective and reversible capture of CO_2.

This work focuses on studies of the process of CO_2 exchange between the chemically-bound, viz. reacted, and unreacted states in the mixture of CO_2 and the ILs. The IL chosen for these studies is composed of the cation $[(CH_3)_3N(CH_2)_2NH_2]^+$ paired with the $[(CF_3SO_2)_2N]^-$ anion.

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Experimental

The wide-bore 17.6 T Bruker BioSpin spectrometer located at AMRIS, University of Florida was employed to carry out C-13 NMR exchange experiments (EXSY) to investigate an exchange of CO_2 between the reacted and unreacted states. One-dimensional (1D) EXSY sequence [(selective π/2) - π/2 - τ_{mix} - π/2 – Acquisition] with a selective excitation pulse was used.

Results and Discussion

Fig. 1 shows the results of 1D EXSY measurements of the chemical exchange and one-dimensional inversion recovery (1D IR) measurements of the T_1 relaxation of CO_2 [1]. The results show that the chemical exchange occurs on a much shorter time scale than the T_1 relaxation. Hence, the mean residence time of CO_2 in the unreacted state ($t_{unreacted}$) can be estimated from the initial slope of the signal decay using

$$I_{unreacted}(\tau_{mix}) = I_{unreacted}(0)\exp(-\tau_{mix}/t_{unreacted}) \quad [1]$$

where $I_{unreacted}$ is the intensity of the normalized signal of unreacted CO_2 and τ_{mix} is the mixing time.

Conclusions

Residence times of CO_2 molecules in the reacted and unreacted states were measured by 1D EXSY.

Acknowledgements

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References

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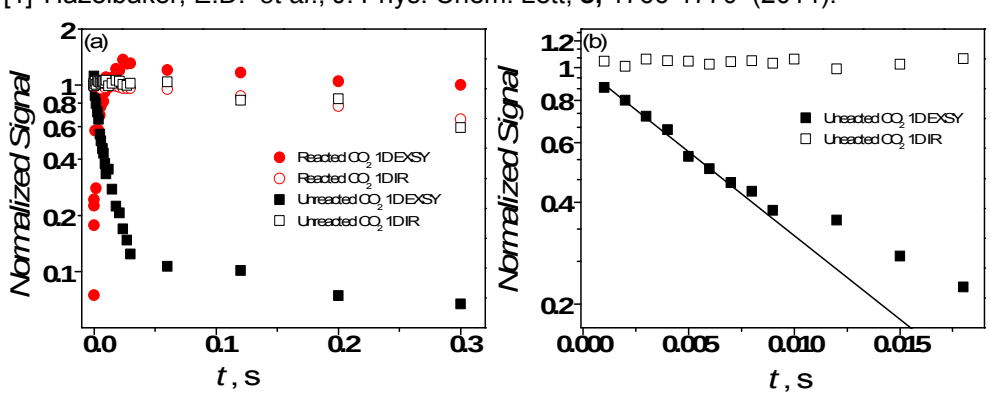

Fig.1 (a) Results of ^{13}C NMR selective 1D EXSY experiments where the selective π/2 pulse was applied for the on-resonance spins of the unreacted carbon dioxide at 125 ppm. Also shown for comparison are the corresponding data obtained by a standard one-dimensional inversion recovery (1D IR) pulse sequence. (b) The same data for the line of the unreacted carbon dioxide at 125 ppm as in (a) shown for a smaller range of mixing times. Solid line shows the best fit of the exchange data for $I_{unreacted}(\tau_{mix})/I_{unreacted}(0) \leq 0.5$ to Eq. 1