Transport Properties of Mixtures of Room Temperature Ionic Liquids and Carbon Dioxide: Multinuclear Pulsed Field Gradient NMR Study

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Introduction

Room temperature ionic liquids (ILs) are molten salts, which are liquid at temperatures around room temperature. A large number of ILs exhibit high absorption capacities for light gases, including carbon dioxide. For applications of ILs in separations and/or storage of carbon dioxide, in addition to CO_2 sorption properties, also transport properties of the mixtures of CO_2 and ILs are of high relevance. This project focuses on studies of self-diffusion in two selected ILs and their mixtures with CO_2 for a broad range of temperatures and carbon dioxide content by pulsed field gradient (PFG) NMR.

Experimental

Transport properties of two ionic liquids having very different gas sorption behavior were investigated: [bmim][Tf2N], a well-characterized ionic liquid exhibiting high physical CO_2 solubility, and $(CH_3)_3N\text{-}CH_2CH_2\text{-}NH_2$ [Tf2N], a so-called "task specific" ionic liquid that chemically complexes with CO_2. Diffusion data were obtained by H-1 and 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).

Results and Discussion

PFG NMR technique was applied to study self-diffusion in mixtures of CO_2 and the ionic liquids. For mixtures of CO_2 and [bmim][Tf2N] the temperature dependencies of all species were found to be in agreement with the Arrhenius law (**Figure 1**). For all temperatures used in this work the diffusivity of CO_2 was found to be much larger than the ion diffusivities. The diffusivity of the cation was found to be larger than that of the anion [1]. The latter was explained by the preferential mobility of the cations in the direction of the ring plane. Addition of CO_2 into the ionic liquid was found to increase the ion self-diffusivities. This was attributed to fluidization of the system by CO_2 resulting in a decrease of the mixture density. In mixtures of CO_2 and $(CH_3)_3N\text{-}CH_2CH_2\text{-}NH_2$ [Tf2N] in addition to physiosorbed CO_2 we have also observed chemisorbed CO_2. The latter exhibits the known chemical shift of the carbamate carbonyl group ($^{13}C{=}O$). Our PFG NMR data indicate that there is an exchange between these two types of CO_2 species on the time scale of tens of milliseconds. The exchange is manifested by the observed dependence of the apparent diffusivities of these species on diffusion time.

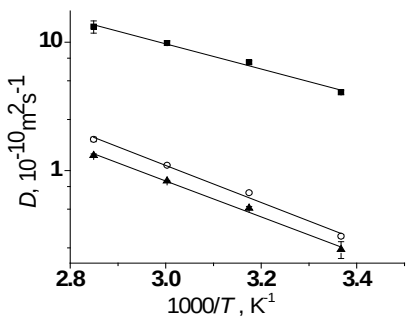

Figure 1. Examples of the measured temperature dependencies of the self-diffusivity of the [bmim] cation (○), the [Tf2N] anion (▲), and carbon dioxide (■) in the mixtures of [bmim][Tf2N] and CO_2. The number of carbon dioxide molecules per anion-cation pair is 0.063.

Conclusions

It is demonstrated that high field, high gradient PFG NMR allows obtaining unique data on transport properties of mixtures of CO_2 and ILs.

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References

[1] Hazelbaker, E.D., *et al.*, J. Phys. Chem. B **116**, 9141–9151 (2012).