Probing Free Volume and Gas Solubility in Silicon-Functionalized Ionic Liquids

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The design of ionic liquids (ILs) with tailored free volumes and selective gas absorption properties is critical to advancing sustainable industrial processes, including gas separation and transformation. In a joint experimental and computational study, we investigate the role of silicon-functionalized sidechains in imidazolium-based ILs, demonstrating their capacity to yield fluids of exceptionally low density and viscosity, properties that are promising for gas capture due to their enhanced free volume. [1] By employing argon as a noninteracting probe, we quantify the relative free volumes in these systems, revealing that silicon-based branching with alkylsilane and siloxane groups enhances argon solubility compared to carbon-based analogues, though anion size remains the dominant factor. Using classical MD simulations with the CL&Pol polarizable force field, [2] we demonstrate similarities between cavity and argon local environments in ILs, confirming argon as a good probe for free volume analysis. Our approach enables the identification of the IL with the highest gas solubility without the need for computationally expensive free energy calculations or costly experiments. Building on these insights, we extend our analysis to the absorption of small hydrocarbon gases, such as ethylene and acetylene, and elucidate the molecular mechanisms by decomposing the residual chemical potential into van der Waals, electrostatic, and polarization contributions. We also demonstrate that, unlike ethylene, acetylene solubilities are influenced by specific interactions with IL ions, such as the formation of H-bonds with anions and enhanced π-stacking with the imidazolium cation. Our findings identify IL structural features that determine absorption thermodynamics and propose design rules for next-generation sorbents for a range of applications.

Keywords:
Ionic liquids, free volume, gaseous solutes, solubility, molecular dynamics, polarizable force field

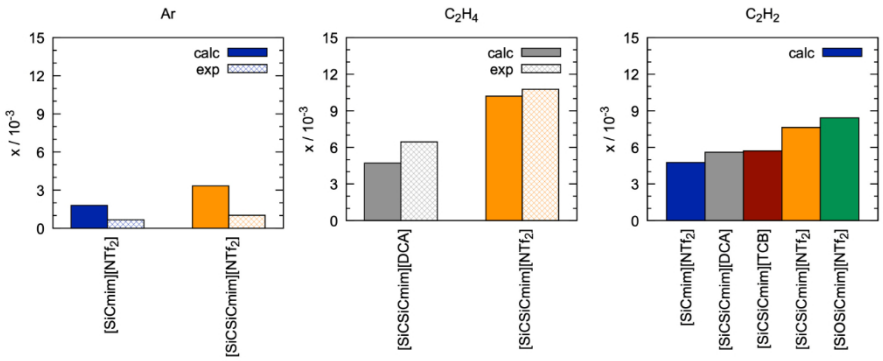

Figure 1. Experimental and calculated solubilities of argon, ethylene and acetylene in Si-functionalized ILs

References:

[1] E. Bakis et al., Chem. Sci. 2022, 23 (31), 9062.
[2] Goloviznina et al., J. Chem. Theory Comput. 2019, 15 (11), 5858.