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Experimental and theoretical study of free volume in silicon-functionalized ionic liquids

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Due to the dominating Coulombic interactions, packing of ions in ionic liquids (ILs) solely depends on ion shape and size. The free volume in ILs is thus generally smaller than in molecular liquids. The low volatility and structural tuneability of ILs make them attractive for applications involving gaseous solutes. Greater free volume can entropically contribute to absorption of gases and, for example, allow selective absorption based on size when other solvent-solute interactions are of comparable energy. Understanding of design principles for ILs of higher free volume is therefore crucial towards efficient IL-based materials for gas capture and separation.

In this work we have designed, prepared and characterised new heavily branched ILs containing several silicon atoms within the cation. Dicyanamide [N(CN)2]-, tetracyanoborate [B(CN)4]- and bis-(trifluoromethanesulfonyl)imide [NTf2]- were selected as anions due to differences in their size and rigidity. Argon absorption was measured in 9 ILs using a low-pressure isochoric saturation method, and the mole fraction □(Ar) solubilities were used as probe for relative free volumes. In order to validate experimental results and explore argon solvation environment, molecular dynamics simulations were performed utilizing the recently developed CL&Pol polarizable force-field.

Branching in the carbon atom chain leads to significant increase in IL viscosity compared to the linear counterparts, while silicon atom incorporation in their isoelectronic analogues provided a remarkable viscosity reduction. Modelling of cavity size distribution via MD provided a set of argon solubility data that matched the order of experimental solubility measurements. Results of this study demonstrate the usefulness of the methodology of probing and prediction of the free volume in ILs, and shed light on the structural features leading to increased free volume and reduced IL viscosity.

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