Fluorescence Correlation Spectroscopy Evidence for Structural Heterogeneity in Ionic Liquids

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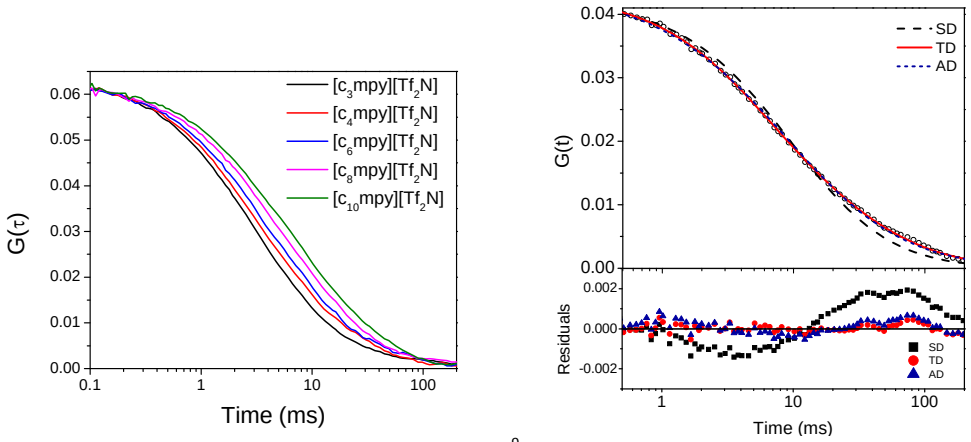
Achievement

The existence of self-aggregation in room temperature ionic liquids (RTILs) has been a subject of intense interest in recent years. Prepeaks or first sharp diffraction peaks (FSDPs) at q = 0.2–0.5 $Å^{-1}$were observed for RTILs using x-ray and neutron scattering techniques. However, the origin of these FSDPs has been a subject of extensive debate recently. In this work, we provide new experimental evidence for chain length-dependent self-aggregation in RTILs using fluorescence correlation spectroscopy (FCS). In studying a homologous series of *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_nMPy][Tf_2N], RTILs of varying alkyl chain length (*n* = 3, 4, 6, 8, and 10), biphasic solute diffusion dynamics were observed; both the fast and slow diffusion coefficients decrease with increasing alkyl chain length, with the relative contribution from slower diffusion increasing for longer-chained [C_nMPy][Tf_2N]. Biphasic diffusion dynamics are explained by self-aggregation of the nonpolar alkyl chains in the cationic [C_nMPy]$^+$.



(Left) Normalized autocorrelation curves for 2.5 × 10^{-9} nM R6G in [C_nMPy][Tf_2N] for *n* = 3, 4, 6, 8, and 10. (right) Fits for the autocorrelation curves for R6G in [C_8MPy][Tf_2N] by use of three diffusion model.

Significance

Through FCS studies, self aggregation of the non-polar alkyl chains in the cationic [C_nMPy]$^+$ is observed. This provided us additional experimental evidence to unravel the mysteries of structural heterogeneity in ionic liquid. This work accords with previous MD simulations and scattering results indicating self-aggregation in RTILs and provides important insight into the local solvent structure, which plays a pivotal role in fluid characteristics impacting application in areas as diverse as drug delivery, batteries, fuel cells, and solar cells.

Credit

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