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Dynamic Heterogeneity in Ionic Liquids near and below the Glass Transition: Rotational Diffusion of Probes in 1-Butyl-3-methylimidazolium Hexafluorophosphate FEHMI BARDAK, JUSTIN R. RAJIAN, LARRY G. HINES, RICHARD A. BARTSCH, EDWARD L. QUITEVIS, Texas Tech University — Dynamic heterogeneity in the ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]) (T_g = 196 K) near glass transition is investigated by conducting probe rotational diffusion experiments on rubrene and tetracene in [Bmim][PF_6] using the fluorescence recovery after photobleaching (FRAP) technique. Rotational anisotropy decays for the probes in the temperature range T_g–6 to T_g+4 are well described by the stretched exponential function. The stretching parameter is found to be constant for both probes with $\beta_{tetracene}$ =0.71 and $\beta_{rubrene}$ = 0.88. The viscosity of [Bmim][PF_6] at high temperatures from 353 K to 283 K and near T_g from 203 K to 196 K can be fit by a single VFT equation. In the temperature range of our measurements, the rotational diffusion of these probes in [Bmim][PF_6] is decoupled from structural relaxation with a rotational correlation time following a fractional Debye-Stokes-Einstein (DSE) relation.

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