

Fast fluctuations in deep eutectic melts: Multi-probe fluorescence measurements and all-atom molecular dynamics simulation study

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ABSTRACT

Larger excitation wavelength dependence of fluorescence emission of chromophores with shorter lifetime suggests fast environmental fluctuations in $(\text{CH}_3\text{CONH}_2 + \text{LiBr}/\text{NO}_3)$ deep eutectics. Stronger fractional viscosity dependence for rotation of a short-lifetime probe has been observed and ascribed to stronger sensitivity to these fast fluctuations. All-atom molecular dynamics simulations reveal stretched exponential relaxation for the wavenumber dependent incoherent and coherent scattering functions for acetamide with dominating sub-hundred picosecond and sub-nanosecond timescales. These simulated results provide support to the experimentally observed different fractional viscosity dependence of rotation rates for probes with different lifetimes, and stronger decoupling for short-lifetime probes in these melts.

1. Introduction

Micro-heterogeneity in solution structure of (amide + electrolyte) deep eutectic (DU) melts is known for a long time [1–4]. However, characterization of this micro-heterogeneity and understanding its impact on a chemical event occurring in these media are still at the developing stage [5–8]. Dielectric relaxation measurements extending up to 100 MHz frequency range have reported pronounced non-Debye relaxation mechanism with extremely slow timescales, suggesting collective nature of the relaxation [4]. The length-scale involved in such collective relaxation has not been understood in terms of spatial correlations as scattering measurements using radiations of atomic resolution have not been performed yet. Recent fluorescence measurements [5–7] have explored solution structure and dynamics of several (acetamide + electrolyte) deep eutectics where pronounced excitation wavelength (λ_{exc}) dependence of fluorescence emission of a dissolved solute and a strong decoupling between solute rotation rate and medium viscosity have been observed. The above decoupling is manifested via fractional viscosity dependence of the measured average rotation time, $\langle\tau_r\rangle \propto \eta^p$, with p much less than unity. Similar fraction power dependence on viscosity has also been observed for the average time for solute solvation with fraction power less than the corresponding p obtained for solute rotation. The latter may be interpreted as a sort of translation-rotation decoupling [9–13]. The fractional viscosity dependence and the translation-rotation decoupling mentioned above, which resemble closely to those for deeply super-cooled liquids [14–16], have been

attributed to the dynamic (temporal) heterogeneity of these DU melts. A model computer simulation study predicts strong dynamic heterogeneity via pronounced non-Gaussian character of particle displacement in these complex melts and collective blockage of ion movement [8]. In addition, the simulated diffusion coefficients have been found to be larger than those predicted by hydrodynamics using experimental viscosity as input, hinting at diffusion-viscosity decoupling in these DU melts.

In such a scenario the recent fluorescence results [7] on DU melt, $[0.78\text{CH}_3\text{CONH}_2 + 0.22\{f\text{LiBr} + (1-f)\text{LiNO}_3\}]$ appear to be more interesting as fluorescence emission of coumarin 153 (C153) exhibits significant λ_{exc} dependence which was absent in $[\text{CH}_3\text{CONH}_2 + \text{K}/\text{NaSCN}]$ melts [6], suggesting more extensive solute-sensing of inhomogeneous density fluctuations in presence of lithium salts. This is further supported by the more pronounced fractional viscosity dependence of solute solvation and rotation rates in DU containing lithium salts than in presence of thiocyanates. The scenario turns out to be even more interesting as both the spatial (λ_{exc} dependence) and temporal (η^p dependence) heterogeneities exhibit Br^- ion concentration dependence which becomes stronger with a solute having excited state lifetime shorter than that of C153. Curiously, λ_{exc} dependence has been found to be dominating at the NO_3^- rich region whereas η^p dependence becomes more severe at the Br^- ion enriched composition. These results once again support the view that emergence of temporal heterogeneity does not necessitate observation of spatial heterogeneity [17–19]. For the present melt, this may also mean that inhomogeneous density fluctuation timescales largely remain unchanged across the Br^- ion concentration; it is the competition between the solute lifetime (τ_{life}) and solute density fluctuation that brings out the observed difference in η^p dependence for different solutes. Characterization of this density

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