

Decoupling of Dynamics at Temperatures Much Above Glass-Transition Temperature: (Amide+ Electrolyte) Deep Eutectics

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Abstract:

Time-resolved fluorescence Stokes shift and anisotropy measurements using a solvation probe in $[0.78\text{CH}_3\text{CONH}_2 + 0.22\{f \text{LiBr} + (1-f) \text{LiNO}_3\}]$ melts reveal a strong decoupling of medium dynamics from viscosity. Interestingly, this decoupling has been found to occur at temperatures ~ 50 - 100 K above the glass transition temperatures of the above melt at various anion concentrations (f). The decoupling is reflected via the following fractional viscosity dependence (α) of the measured average solvation and rotation times (τ_s and τ_r , respectively): (τ_s being solvation or rotation), with α covering the range $0 < \alpha < 1$. Although this is very similar to what is known for deeply supercooled liquids, it is very surprising because of the temperature range at which the above decoupling occurs for these molten mixtures. The kinship to the supercooled liquids is further exhibited via τ_s/τ_r which remains always larger for τ_s than for τ_r , indicating a sort of translation-rotation decoupling. Multiple probes have been used in steady state fluorescence measurements to explore the extent of static heterogeneity. Estimated experimental dynamic Stokes' shift for coumarin 153 in these mixtures lies in the range 1000 - 1500 cm $^{-1}$, and is in semi-quantitative agreement with predictions from our semi-molecular theory. The participation of the fluctuating density modes at various length-scales to the observed solvation times has also been investigated.