# **Observation of Microheterogeneity in Highly Concentrated Nonaqueous Electrolyte Solutions**

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**Supporting Information** 

ABSTRACT: The development of models to describe structure and dynamics of nonaqueous electrolyte solutions is challenging, and experimental observations are needed to form a foundation. Here, neutron scattering is used to probe molecular dynamics in nonaqueous organic electrolytes. Two solutions were compared: one contained symmetrical electrolyte molecules prone to crystallize, and one contained desymmetrized electrolyte molecules preferring disordered states. For the latter, calorimetry and neutron data show that a disordered fluid persists to very low temperatures at high concentrations. Upon heating, localized cold crystallization occurs, leading to burst nucleation of microcrystalline solids within fluid phases. Our findings indicate molecular clustering and point to solvation inhomogeneities and molecular crowding in these concentrated fluids.

Molecular structure and dynamics of nonaqueous electrolytes are poorly understood, especially for highconcentration and/or multicomponent systems. The solvation environment involves neutral and charged solute molecules, ionic species, and solvent molecules. Understanding this environment at all length scales, time scales, and states-ofcharge is important from both fundamental and technological perspectives. Angell and Sare were early proponents of understanding low-temperature electrolyte behavior as a basis for liquid-state theory of concentrated aqueous electrolyte solutions.<sup>1</sup> Their general findings apply to both aqueous and nonaqueous electrolytes. Low-temperature <sup>1</sup>H NMR measurements of metal cations in aqueous and nonaqueous solutions distinguished cation solvation signals from bulk solvent, inferring the solvation shell structure around the cation.<sup>2</sup> Molecular dynamics and low-temperature behavior of highly concentrated fluids piques fundamental and practically relevant questions such as how rearrangement of molecular charges affects clustering and nucleation/solubility and connections between thermodynamic state and mass transport. Primitive computational models of electrolytes range from binary sizesymmetric systems, with constrained electrolyte charge/size,<sup>3</sup> to more realistic Monte Carlo simulations of size-asymmetric electrolytes that suggest greater clustering than size-symmetric models predict.<sup>4</sup> Most models do not consider the multicomponent nature common to nonaqueous electrolyte systems.

Generally, organic-based systems contain one or more redox-active organic molecules (ROMs) and a supporting electrolyte like lithium bis(trifluoromethane)sulfonimide (LiTFSI). LiTFSI, commonly found in ionic liquids, favors the persistence of fluid phases down to low temperatures and vitrification to amorphous solids.<sup>5</sup> Electrolyte fluids should maintain flow while maximizing concentration.<sup>6</sup> Some have

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suggested utilizing ROMs with melting temperatures near room temperature facilitates high concentrations.<sup>7</sup> However, increased concentration impedes flow through heightened electrolyte viscosity, cell resistance, and possibility of solids formation.<sup>8,9</sup> Technical advances will benefit from a general model for complex fluids, but this generalization has lagged behind simple binary electrolytes. One recent report correlated dynamics and ROM solvation environment where small equivalence of water had significant benefits.<sup>10</sup> Such nuances motivate our pursuit of improved fundamental modeling as multicomponent nonaqueous electrolyte systems deviate from traditional homogeneous/continuum behavior.

Here, neutron scattering is used to probe the nanosecondscale dynamics of complex electrolytes at different temperatures to elicit subtle changes in metastability and corresponding high-concentration limits. Selectively deuterated ROMs (i.e., "hidden" ROMs, with minimized incoherent neutron scattering) allow highlighting a desired chemical species (the protiated "visible" component). We examine ROM fluids containing a catholyte (oxidized species), an anolyte (reduced species), and supporting electrolyte (LiTFSI) as an indirect but sensitive indicator of molecular structure. We chose two model systems derived from 1,4-dialkoxybenzene, a popular catholyte family. One system contained a highly symmetric molecule, 1,4-dimethoxybenzene (DMB), while a second contained a desymmetrized molecule, 2,5-di-tert-butyl-1methoxy-4-[2'-methoxyethoxy]benzene (DBMMB). 2,1,3-Benzothiadiazole (BzNSN) was used as an anolyte. Differential scanning calorimetry (DSC) of individual and mixed ROM solutions with or without LiTFSI was measured to supplement the neutron scattering data (see the Supporting Information).

Incoherent elastic neutron scattering temperature scans were first performed to examine dynamics from fast atomic motion. The elastic scattering is dominated by the incoherent scattering for protiated ROMs, and the scattering intensity is proportional to the effective Debye–Waller factor, from which we obtain the mean squared displacement (MSD).<sup>11–13</sup>

Figure 1 shows the extracted MSD during the temperature scan. The control LiTFSI solution (yellow asterisks) exhibits abrupt changes of  $\approx 6$  Å<sup>2</sup> on cooling and heating with a hysteresis of ~15 K. These features are attributed to CD<sub>3</sub>CN crystallization, as suggested by DSC (see Figure S1). The hysteresis may be from strong association of solvent with Li<sup>+</sup> ions that causes freezing point depression and supercooling. The solutions of BzNSN (with masked DMB- $d_{10}$ , purple circles) or DMB (with masked BzNSN- $d_4$ , green squares) also exhibit features that at 0.5 M coincide in temperature with CD<sub>3</sub>CN crystallization (Figure 1a) but shift at 1.0 and 1.5 M (Figure 1b,c, respectively), giving ~40 K separation between the two transitions at 1.5 M. At this concentration, the crystallization of ROMs from solution occurs ~250 K, and the corresponding melting events of DMB and BzNSN on warming each have hysteresis of ~25 K.

Similar crystallization/melting events are observed by DSC for protiated DMB/BzNSN/LiTFSI solutions, with additional crystallization/melting of LiTFSI, which is unobserved by neutrons (see Figure S4a). Crystallization occurs in DMB and BzNSN control solutions with and without LiTFSI, with more monotropic behavior observed with LiTFSI (for DSC, see Figures S2 and S3).

The tendency of these aromatic molecules to crystallize is expected from  $\pi$ -stacking.<sup>15</sup> DMB can form macroscopic crystals<sup>16</sup> where the molecules arrange in parallel planes with



**Figure 1.** Expanded elastic fixed-window scans fitted to the MSD of BzNSN (purple circles) and DMB (green squares) at 0.5, 1.0, and 1.5 M recorded upon heating (dark curves) and cooling (faded curves). All samples contain 1.0 M LiTFSI in CD<sub>3</sub>CN. The control solution is 1.0 M LiTFSI in CD<sub>3</sub>CN (yellow asterisks).

alternating arene rings. The carbon atoms of the methoxy groups have significant double bond character,<sup>17</sup> and likely contributions from p electrons favor an extended planar system as an energy minimum.<sup>18</sup> BzNSN molecules readily form crystals by  $\pi - \pi$  stacking and intermolecular coordination of N and S atoms.<sup>19–21</sup> These relatively strong interactions reduce entropic costs associated with crystallization.<sup>22</sup>

In contrast, structural features of DBMMB impede crystallization; it is a neat liquid at 295 K. tert-Butyl groups prevent  $\pi - \pi$  stacking and provide steric shielding as unsubstituted oxidized DMB is chemically unstable,<sup>2</sup> while the methoxyethoxy group provides a nonzero dipole moment and depresses melting. DSC of DBMMB-containing solutions also reveals a different molecular picture. In DBMMB solutions with no LiTFSI, crystallization occurs as a single exotherm on cooling for all concentrations (see Figure S2c). However, with 1.0 M LiTFSI, no crystallization is observed on cooling for all concentrations, and the solutions are supercooled (to the DSC cooling limits, 180 K, see Figure S3c). On heating, some broad events are observed including possible cold crystallization. Nevertheless, DBMMB and LiTFSI in combination induce more eutectic-like properties and disfavor crystallization. Even with BzNSN, supercooling remains (Figure S4b), and a reversible glass transition at ~190 K is observed at 1.5 M; at 1.0 and 1.5 M, a cold crystallization event appears at ~260 K on heating.

The DMB and DBMMB solution-phase crystallization differences are rationalized by nucleation theory.<sup>26</sup> In nucleation theory, the free energy of nucleation balances negative free energy gains from crystal size with positive free energy losses from surface interactions with the solution. Figure 2 shows landscapes for nucleation of DMB or DBMMB from a multicomponent electrolyte solution. Ease of molecular



Figure 2. Postulated free energy profiles in solutions of DBMMB vs DMB. More efficient packing of DMB molecules results in a lower free energy barrier (green dotted line) while steric effects and larger size decrease DBMMB's packing density, raising the free energy barrier (blue solid line). Additional solvation between ethereal oxygen atoms in DBMMB and lithium stabilize the intermediate supercooled phase, creating a potential energy well.

packing in DMB increases the density of aggregates and lowers the barrier to crystallization, while the bulk of DBMMB impedes compact organization and increases the free energy. DBMMB likely follows a two-step nucleation with a stabilized supercooled phase in the nucleation reaction coordinate. Lithium solvate formation<sup>27</sup> also stabilizes the supercooled state of DBMMB as supercooling is not observed without LiTFSI. Conversely, the methoxy groups in DMB only have weak, transient interactions with lithium.

To further complete this molecular picture, we examined the elastic scattering for DBMMB (masked BzNSN- $d_4$ ) and the extracted MSD (Figure 3). As observed in DSC, these solutions are supercooled and markedly different from the results in Figure 1. The 0.5 M DBMMB (Figure 3a) had only small MSD transitions overlapping with CD<sub>3</sub>CN crystallization of the control solution. At higher concentrations, the electrolytes and solvent did not crystallize at all, instead forming supercooled solutions (Figure 3b,c, cooling curves); only little melting was observed on subsequent heating of these solutions. Expanded MSD insets (Figure 3d) show intricate differences between ROM concentrations. While the 0.5 M sample has a feature corresponding to CD<sub>3</sub>CN melting (224 K), the 1.0 M shows additional evidence for a cold crystallization,<sup>28</sup> indicated by a slight dip in the MSD at 227 K after the small CD<sub>3</sub>CN melting event (222 K). For 1.5 M, multiple small-amplitude meltings are observed on heating. To obtain insight into these transformations, quasi-elastic neutron scattering (QENS) was used.

We used QENS to study the molecular-level differences in the DBMMB electrolyte phases observed. The 1.0 M DBMMB sample was chosen due to its unexpected cold crystallization. By analyzing the QENS spectra (see Figure 4 and the SI), we can extract the Q-dependence of the relaxation time  $\tau$ . Figure 4 shows the fitted QENS spectra at three Q values for 1.0 M DBMMB. All spectra are at 250 K but are measured either after cooling or heating to 250 K as in the fixed-window scan (i.e., the system is supercooled or post-cold crystallization). In the spectra obtained after cooling, the elastic scattering component of the fit is weak. As Q decreases, the line becomes broadened, indicating faster dynamics. Conversely, the spectra obtained after heating have narrower peaks, and there is little change with decreasing Q. Here, both elastic and inelastic scattering components are present, revealing that the probed molecules move more slowly on heating than cooling. In a plot of relaxation rate  $(1/\tau)$  vs  $Q^2$  (Figure 5a), after cooling, the rate increases nearly linearly with  $Q^2$  but deviates slightly from



Communication

Inset Range: 200–250 K

**Figure 3.** Expanded elastic fixed-window scans fitted to the MSD of DBMMB (blue stars) at 0.5, 1.0, and 1.5 M in  $CD_3CN$  recorded upon heating (dark curves) and cooling (faded curves). All samples contain 1.0 M LiTFSI in  $CD_3CN$ . The control solution is 1.0 M LiTFSI in  $CD_3CN$  (yellow asterisks). Panel d highlights details from 200–250 K.

linearity at large Q. This behavior can be described by the Singwi–Sjölander jump diffusion model,<sup>29–31</sup> where the jump distance follows a distribution, implying unrestricted homogeneous diffusion with random jumps in the supercooled liquid state. The corresponding diffusion coefficient extracted from the model is  $10.7 \pm 1.1$  Å<sup>2</sup>/ns, and the residence time is 0.025

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**Figure 4.** QENS spectra of 1.0 M DBMMB at 250 K. The solution is cycled as in the fixed-window scan with isothermal holds at 250 K for the measurement on cooling or heating. The overall fit (orange line) is the sum of the elastic (ENS, green dotted line) and inelastic (QENS, dark purple dashed line) contributions. For cooling  $\beta = 0.65$ , while for heating  $\beta = 0.5$ . Error bars throughout the text represent standard error.

 $\pm$  0.005 ns, which gives an average jump distance of ~1.3 Å extremely local. After heating, the relaxation rate is linear with  $Q^2$  only at very small Q (<0.5 Å<sup>-1</sup>). Beyond, the Q-dependence of the rate has oscillatory behavior (Figure 5b), suggesting a different mechanism. Here, we apply the Chudley–Elliott jump diffusion model,<sup>32</sup> where the jump distance is fixed to describe the diffusion of liquids with short-range order. The fitted residence time increases to 0.120  $\pm$  0.024 ns, indicating much slower dynamics, and the jump length is ~6.1 Å, much longer than the supercooled liquid, indicating a more-ordered local structure (for details, see the SI). This latter result suggests there are both liquid-like and solid-like microdomains, the latter resulting from burst nucleation after the cold crystallization.

These results agree with our interpretation of the fixedwindow scan of 1.0 M DBMMB. At 250 K, the Q-dependence after the cooling cycle is typical for a supercooled liquid (strong Q-dependence), while heating to the same temperature results in mixed dynamics (weak Q-dependence). Thus, the two regions highlighted in Figure 5c have markedly different dynamics depending on heating direction. These results demonstrate how seemingly minor structural changes in electrolyte design lead to perturbative phase changes and the



**Figure 5.** (a) 1.0 M DBMMB at 250 K follows the Singwi–Sjölander jump diffusion model after cooling, suggesting a more homogeneous phase, and (b) the Chudley–Elliott jump diffusion model after heating, suggesting mixed solid-like microcrystalline and liquid-like domains; (c) cartoon denoting these regimes.

delicate balance between maintaining an amorphous glassy state versus unwanted crystallization.

In summary, we used neutron scattering and DSC measurements to probe the dynamics and phase behavior in complex functional fluids: concentrated electrolytes containing redox-active molecules. A desymmetrized catholyte molecule, DBMMB, showed the formation of surprisingly stable supercooled solutions and spontaneous crystallization on heating. Our analyses indicate that the solution undergoes a nucleation event from a metastable state to mixed solid-like and liquid-like domains, which causes slower translational diffusion of the molecule. We surmise that the ability of neutron scattering to detect early-onset heterogeneity is highly useful for establishing practical limitations for crowded nonaqueous electrolytes. Further, as more complex electrolytes<sup>33,34</sup> are proposed, fundamental development of crowded electrolyte models will elicit rational in silico prediction of nonaqueous solvation and high-concentration environments.

## ASSOCIATED CONTENT

### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b02323.

Synthetic procedures and experimental characterization data (NMR and HRMS) of synthesized deuterated electrolytes, detailed neutron scattering procedure, DSC data, full fixed-window scans, detailed MSD and QENS fitting equations, relaxation time fitting based on the jump diffusion model, and QENS spectra for each wavevector Q (PDF)

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#### Notes

The authors declare no competing financial interest.

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