

**Combined NMR and Molecular Dynamics Modeling
Study of Transport Properties in Sulfonamide Based
Deep Eutectic Lithium Electrolytes. 1. LiTFSI Based
Binary Systems**

Electronic Supplementary Information:

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Figures S-1 through S-4 display the volume integrals $G(R)$, for the lithium- nitrogen (Figs. S-1 and S-2) and lithium-oxygen interactions. They help to further detail the discussion of the coordination environments surrounding the lithium cations.

From Figs. S-1a and S-2a one can draw a contrast between the monodentate and bidentate coordinations on one hand, and the direct nitrogen coordination on the other. A comparison is made for the coordination number from the second plateau (monodentate/bidentate) versus the first (direct nitrogen coordination). This proportion is roughly 10:1 for nitrogen atoms being in an indirect versus a direct bonding environment. Furthermore, it appears that direct nitrogen coordination via MSA is found for one in every 10-20 lithium cations. This confirms that oxygen coordination is the predominant mode of interaction. The volume integrals for the lithium-oxygen coordination are shown in Figures S-3 and S-4 and have a number of similarities. However, a key difference is in the coordination number of lithium with respect to DMMSA versus MSA. At a 1:1 solvent:salt ratio there exists coordination of approximately 1.5 oxygen atoms from the organic components in both cases. However, at 6:1 solvent:salt ratio the oxygen coordination number for DMMSA is ~ 4.1 , whereas for MSA it approaches 5 oxygen atoms. This can be explained by the smaller size of MSA and the increased mixture density when compared to the DMMSA based mixtures.

Figure 5 uses previously reported conductivity measurements [28] in combination with the diffusion coefficients by NMR, to address the issue of ionicity. The ratio between the conductivity measured by impedance spectroscopy versus that measured via NMR using the Nernst-Einstein relation is in line with the expectations outlined in the paper. Specifically, while significant ion pairing can be observed, its magnitude mirrors the trends observed in transport number. The 3:1 MSA:LiTFSI composition has the greatest degree of ionicity with a lithium transport number ranging from 0.625 to 0.6 over the temperature range of the measurements. This is in contrast to the 6:1

DMMSA:LiTFSI mixture, where the ionicity is lowest and the transport number ranges from 0.40 to 0.35 over the investigated temperature range. These results provide further confirmation that the introduction a hydrogen bonding component can mitigate ion pairing, albeit at the expense of overall conductivity.

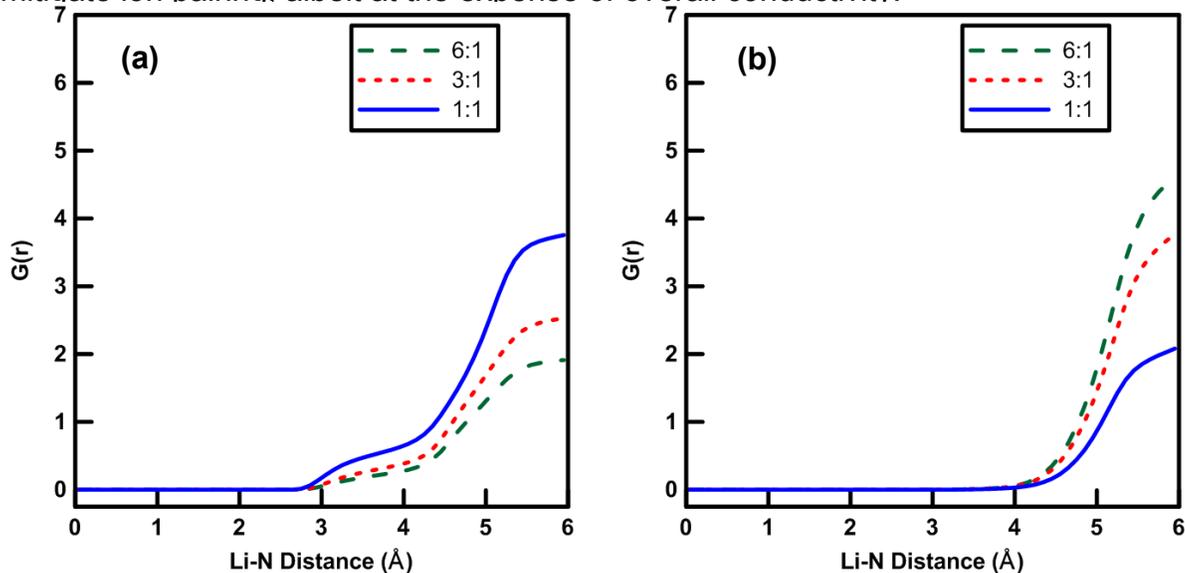


Figure S-1: Lithium-nitrogen volume integrals for Li^+ contact with TFSI^- (a) and DMMSA (b) in DMMSA:LiTFSI mixtures at 298 K.

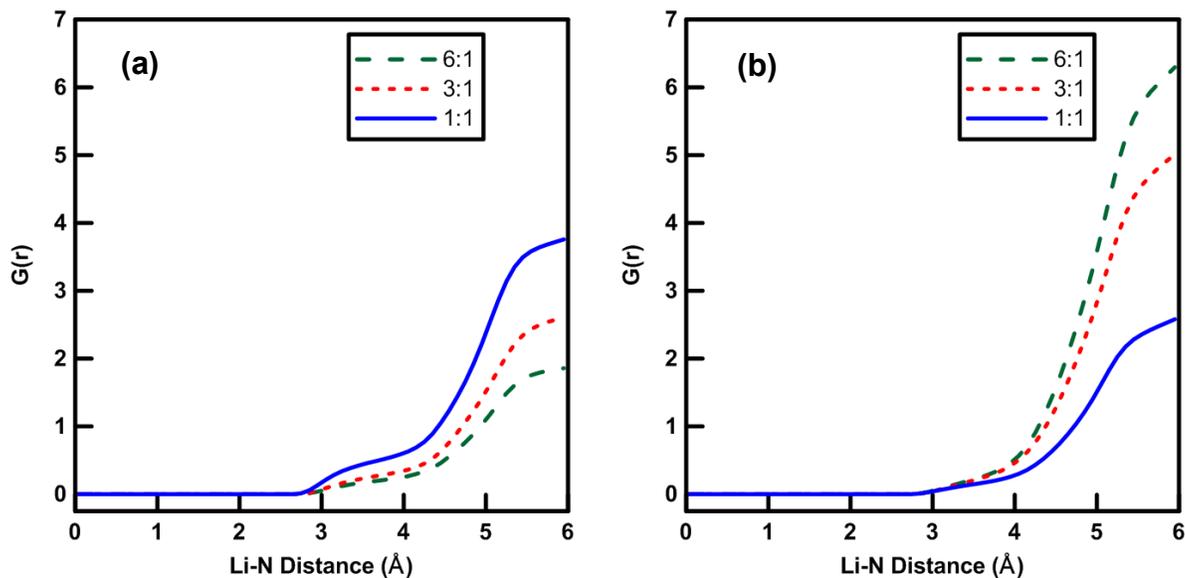


Figure S-2: Lithium-nitrogen volume integrals for Li^+ contact with TFSI^- (a) and MSA (b) in MSA:LiTFSI mixtures at 298K.

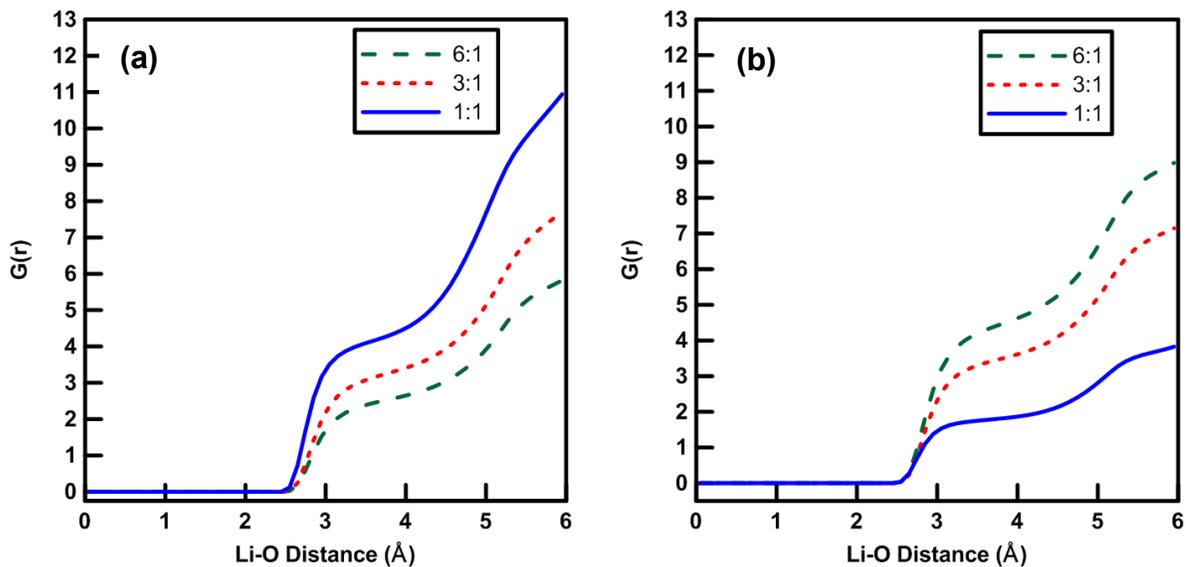


Figure S-3: Lithium – oxygen volume integrals for intermolecular contact between Li⁺ and TFSI⁻ (a) or DMMSA (b) for DMMSA:LiTFSI mixtures at 298 K.

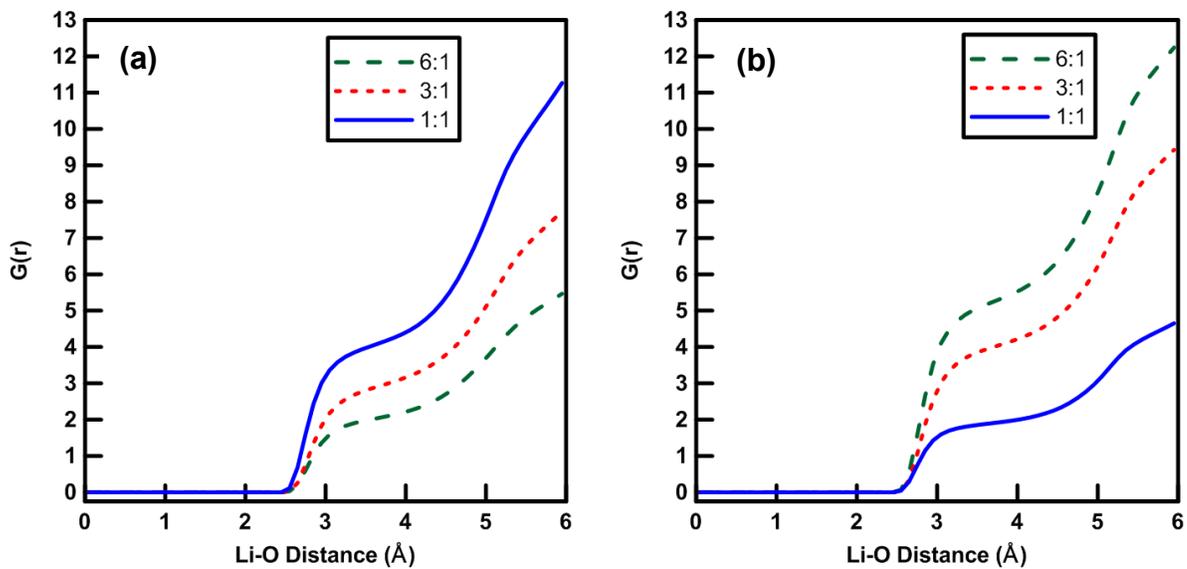


Figure S-4: Lithium – oxygen volume integrals for intermolecular contact between Li^+ and TFSI^- (a) or MSA (b) for MSA:LiTFSI mixtures at 298 K.

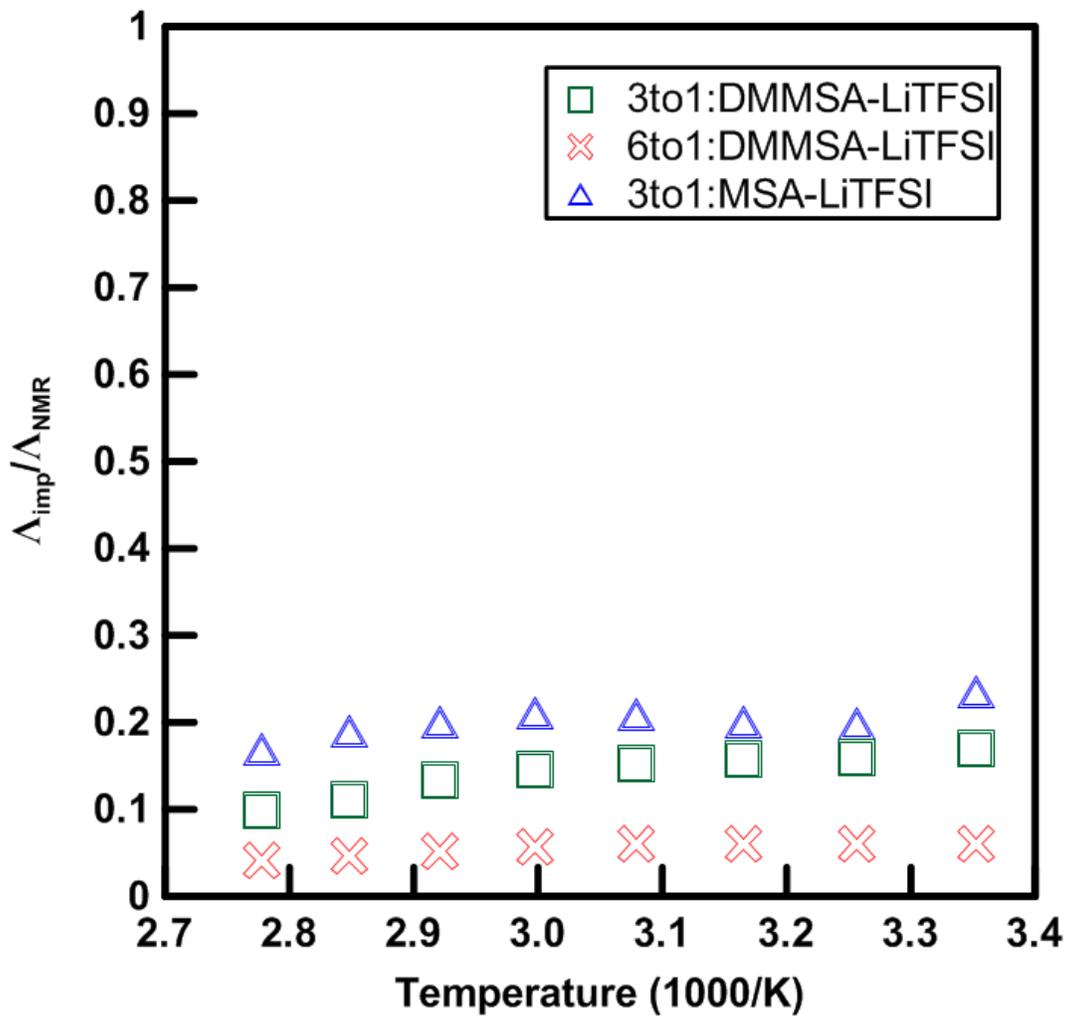


Figure S-5: Ionicity derived through the ratio of molar conductivities, as determined by impedance spectroscopy and NMR.