

# LiBETI Solvate Structures and Ionic Association Interactions in Electrolytes

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The conductivity mechanisms of concentrated electrolytes remain poorly understood. This is especially true of non-aqueous electrolytes in which the low acceptor numbers of aprotic solvents indicate that anion solvation does not occur. Rather, solvation occurs by the competitive coordination of the cations by the solvent donor atoms and counter anions.

In recent years, a class of lithium salts based on fluorinated sulfonyl imide anions,  $[N(SO_2C_nF_{2n+1})(SO_2C_mF_{2m+1})]^-$ , has drawn increasing attention due to the favorable properties of these salts in electrolytes for lithium batteries. The negative charge in such anions (i.e., TFSI<sup>-</sup> or  $[N(SO_2CF_3)_2]^-$ ) is extensively delocalized resulting in weak cation-anion interactions. Unfortunately, corrosion of aluminum current collectors occurs in liquid electrolytes containing LiTFSI [1]. The larger imide analogue BETI<sup>-</sup>,  $[N(SO_2C_2F_5)_2]^-$ , however, exhibits much better passivation of aluminum leading to improved stability [2-4].

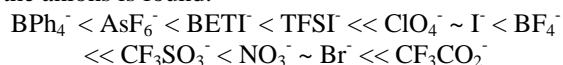
The BETI<sup>-</sup> and TFSI<sup>-</sup> anions are very similar structurally. To better understand the physical properties of concentrated solvent-salt mixtures, insight into the interionic and ion-solvent interactions is necessary. Raman and IR spectroscopy have proven valuable for gleaned information regarding solvate structures in amorphous liquid and polymer electrolytes [5-7]. A much less utilized technique is the determination of crystalline solvate structures [8,9].

Phase diagrams have been prepared for a number of low molecular weight poly(ethylene oxide) glyme-LiBETI systems. Other salt systems (e.g., LiAsF<sub>6</sub>, LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, etc.) were also examined. Two LiBETI solvate structures, (monoglyme)<sub>1</sub>:LiBETI and low temperature (triglyme)<sub>1</sub>:LiBETI, are reported (Figs. 1 and 2). The former is an aggregate structure while the latter consists of contact ion pairs thus providing direct information about Li<sup>+</sup>...BETI<sup>-</sup> coordination and anion structure. The phase diagrams, however, indicate that other solvent-separated ion pairs solvates, in which the Li<sup>+</sup> cations and BETI<sup>-</sup> anions are not coordinated, preferentially form in more dilute mixtures.

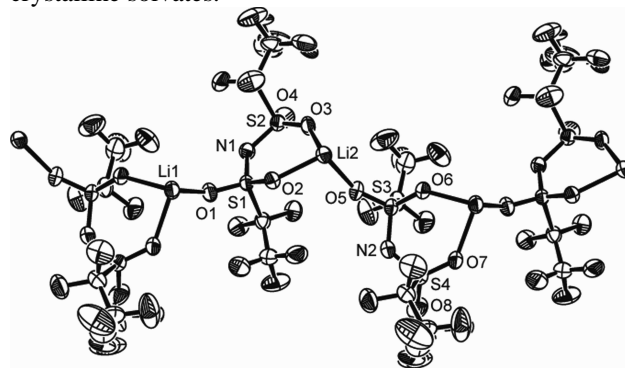
There is strong evidence to suggest that solid state order-disorder phase transitions exist for many of these glyme-LiBETI solvates. This may be associated with rotational motion/disorder of a portion or all of the anions at sub-ambient temperatures. Ab-initio calculations previously reported in the literature have indicated that both the BETI<sup>-</sup> and TFSI<sup>-</sup> anions are highly flexible with two low energy conformations [10,11].

The glyme-LiX diagrams provide information about solvates formed and their thermal stability. The Li<sup>+</sup> cation solvates formed depend both upon the number and structure of solvent coordinating groups as well as the structure and ionic association strength of the anions. Solvate structures thus provide an indirect method of

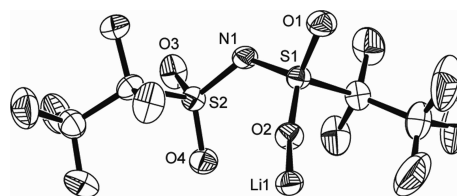
measuring the association strength of a given salt. The following order for increasing ionic association strength of the anions is found:



The thermal stability of the solvates, however, is dictated by more than electrostatic interactions. Anion size, flexibility and structure also play a role. Thus, the BETI<sup>-</sup> and TFSI<sup>-</sup> anions may actually have weaker ionic association interactions with solvated Li<sup>+</sup> cations than AsF<sub>6</sub><sup>-</sup> anions, but the bulkiness and flexibility of the imide anions is disruptive to the favorable packing in the crystalline solvates.



**Fig. 1.** Aggregate structure of the Li<sup>+</sup>...BETI<sup>-</sup> ions in the (monoglyme)<sub>1</sub>:LiBETI solvate.



**Fig. 2.** Contact ion pair structure of the Li<sup>+</sup>...BETI<sup>-</sup> ions in the low temperature (triglyme)<sub>1</sub>:LiBETI solvate.

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