

Ionic transport mechanism in mixtures of protic ionic liquids

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Protic ionic liquids (PILs) exhibit unique transport properties governed by their extensive hydrogen-bonding networks. In this study, we employ computational techniques, specifically polarizable molecular dynamics simulations, to investigate the charge conduction mechanisms in mixtures of PILs with different solvents. Our simulations reveal that the coordination between ions and solvent molecules – mediated through hydrogen bonding – critically influence ionic conductivity, with certain solvents exhibiting anomalous conductivity behavior that does not fit current theories such as the random alloy model [1]. This computational approach provides new insights into the molecular interactions within these mixtures, paving the way for the rational design of new PIL-based systems with enhanced transport properties for applications in electrochemical devices.

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References

1. H. Montes-Campos, S. Kondrat, E. Rilo, O. Cabeza and L. M. Varela, *J. Phys. Chem. C*, 2020, 124 (22), 11754-11759.

Influence of Water on the Transport Properties of Ternary Mixtures with Triglyme and [Li][NTf₂]

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In the engineering of energy storage devices, lithium batteries offer the biggest opportunities regarding energy densities but their electrolytes often have undesirable properties like, for example, a high combustibility [1]. Therefore, possible alternatives to conventional electrolytes are searched for.

Recent studies have shown that by mixing salts consisting of lithium cations and weakly coordinating anions such as NTf₂⁻ with triglyme, so called pseudo-ionic liquids can be formed for certain mixing ratios [2].

Molecular dynamics simulations revealed that by adding triglyme to [Li][NTf₂], the lithium salt changes from contact ion pairs to solvent-separated ion pairs. The lithium cations are coordinated by the oxygen atoms of the triglyme molecules and in consequence, the interaction between anions and cations is weakened leading to improved transport properties of the system.

Hereby, the structural motifs of the cation-triglyme clusters depend almost entirely on the mixing ratio of the two components. For the equimolar mixture, every cation is, on average, enclosed by one triglyme molecule forming a complex with its four oxygen atoms. If the mole fraction of triglyme is further increased, the one-fold triglyme-coordinated state of the cations changes to a two-fold coordination state where two triglyme molecules surround lithium in a double-helical-like manner.

If small amounts of water are additionally added to the different mixtures of [Li][NTf₂] and triglyme, the transport properties such as self-diffusion and viscosity can be further increased. The water molecules intercalate between the cation and the outer oxygen atoms of the coordinating triglyme molecule. The water molecules form coordinative bonds with the cation as well as hydrogen bonds with the detached triglyme oxygen atoms and anions. By this, the water molecules are shielded from each other and should therefore behave chemically different than bulk-phase water. Here, a comparison can be made to water-in-salt electrolytes [3]. At a certain threshold of water content in the ternary mixtures, water starts forming clusters again. At this point, the advantage of adding water diminishes due to the smaller electrochemical window of bulk water [3].

References

- [1] K. Xu, *Chem. Rev.* 2014, 114, 11503–11618.
- [2] K. Ueno, K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, *J. Phys. Chem. B* 2012, 116, 11323–11331.
- [3] A. Triolo, V. Di Lisio, F. Lo Celso, G. B. Appetecchi, B. Fazio, P. Chater, A. Martinelli, F. Scibba, O. Russina, *J. Phys. Chem. B* 2021, 125, 12500–12517.