

**Title: Structural and dynamic properties of pyrrolidinium-based ionic liquid - Li electrolyte solutions**

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Ionic liquids have been proposed to constitute electrolyte solutions that improve the performance of Li-ion batteries, due to their particular properties, especially conductivity. In this work, classical molecular dynamics simulations were used to study the structural and dynamic properties of electrolyte solutions, based on ionic liquids and with different amounts of lithium. Pyrrolidinium cations with small linear chains *1-methyl-1-ethyl pyrrolidinium* (Pyr12) and *1-butyl-1-butyl pyrrolidinium* (Pyr14) were combined with anions *hexafluorophosphate* (PF6) and *tetrafluoroborate* (BF4) to build the pure ionic liquid models, while a fraction of the pyrrolidinium cations were replaced (1:1 proportion) by lithium (Li) cations to form the electrolyte solutions with different fractions of lithium. OPLS-based forcefield parameters as implemented in Gromacs software were used to model the intramolecular and intermolecular interactions of all the species, and all the properties were obtained from a 20 ns production phase with NPT ensemble at 400 K temperature and 1 bar pressure. Our results show that the density of systems with PF6 anions is larger than that of the systems with BF4, for all fractions of lithium. Also, for the four ionic liquids considered, the density decreased almost linearly with the increasing amount of lithium, except for the Li-anion systems (i.e., without pyrrolidinium). We have obtained interesting trends also for the behavior of the pair correlation function ( $g(r)$ ) analyzes and for the cation and anion self-diffusion. Our results show that for systems without lithium, the cations diffuse differently in each ionic liquid, although the systems with the same anion have closer values of cation self-diffusion. Anion self-diffusion depends on the anion species. Lithium diffusion is larger in Pyr12-anion systems, with a 0.25 lithium fraction, and BF4 anions. It is important to point out that the lithium diffusion in the ionic liquid is smaller than the diffusion of other ionic species, as reported in the literature. Our results are of interest for the engineering of new ionic liquid based electrolytes for the batteries of the next generation. This research was developed under the framework of the BAT4EVER project ([www.bat4ever.eu](http://www.bat4ever.eu)) that has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 957225.