Molecular dynamic simulations of concentrated solutions for Lithium-ion batteries

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For the mean time the propylene carbonate (PC) – dymethoxyethane (DME) mixed solvent is considered as an appropriate system for modelling the microscopic structure and ion dynamics in the electrolyte solutions based on cyclic carbonates, linear esters and lithium salts.

In the present work effective force field models of PC and DME molecules were developed for molecular dynamics (MD) simulations of $LiBF_4$ solutions based on PC–DME mixtures. PC and DME molecules were represented by a six-site unpolarizable flexible and a seven-site unpolarizable rigid models, respectively. Partial atomic charges, molecule geometries and dihedral potentials for DME molecule were obtained by quantum-chemical calculations in the media at the B3LYP/aug-cc-pVTZ level of theory in the framework of the reaction field model of the surrounding media.

The MD simulations were performed for pure solvents and their mixtures with a PC molar content of 25%, 50% and 75%, and infinitely diluted, 0.1 M and 1.0 M $LiBF_4$ solutions in these mixtures. The validation of the proposed force field models was done by the comparison of the experimental and calculated limiting molar conductivities (λ_0^i) of the Li^+ and BF_4^- ions.

It was found that Li^+ solvation shell consists of six PC molecules for all the systems under the question excluding pure DME, where the coordination number was found to be equal to six due to the three DME molecules within the first solvation shell.

It was also found that in 0.1 M mixtures the Walden product doesn't depend on the mixed solvent composition ($\lambda_0^i \cdot \eta = \text{const}$) due to a preferential solvation of Lithium cation by six PC molecules.

For 1.0 M $LiBF_4$ solutions in PC special attention paid to the MD simulation of systems with different initial configuration of the ionic subsystem, and to the influence of the association degree on the viscosity and conductivity of electrolyte solutions.