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Transport properties and ion aggregation of $SBPBF_4$ in acetonitrile solutions: experiment vs. molecular modelling

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ABSTRACT

Electric double-layer capacitors (EDLC) are perspective electrochemical storage of electronic energy due to high power density, short time of charge/discharge and long lifetime. The conductivity of electrolyte is critical characteristics of EDLC and therefore decision of new electrolytes is of interest for scientist and engineers as well.

There are many directions of research in order to optimize their working conditions related to the electrolytes and in our work we focus on understanding at the molecular level their conductivity. The chosen electrolytes are solutions of 1-1`-spiropyrrolidiniumtetrafluoroborate acetonitrile ($SBPBF_4$/AN). Indeed, among the variety of aprotic dipolar solvents, acetonitrile (AN) is the most popular solvent for the EDLC application due to its low viscosity, a wide electrochemical window and the ability to dissolve practically important salts. While it was shown recently that $SBPBF_4$ solutions demonstrated a 10% larger conductivity value (in the range of 1-3 M) comparing to methyltriethylammonium tetrafluoroborate ($MTEABF_4$) ones widely used in industry [1,2].

The occurrence of a maximum in conductivity concentration dependence is observed for SBPBF4/AN, similarly for binary mixture of room temperature ionic liquids (RTILs) with molecular solvents [1, 2]. Although the origin of this phenomenon is always related to the ion association at a high electrolyte concentration, the detailed microscopic structure of the ions subsystem is not clearly perceived.

Here we present the detailed investigation of the transport properties and microstructure of an ionic subsystem of highly concentrated solutions $SBPBF_4$ in AN using conductometric experiment and classical molecular dynamics (MD) simulations. With this objective, the new force fields for SBP^+ cation and BF_4^- anion were developed on the basis of quantum chemical calculations.

It has been established that an existence of maxima on concentration dependences of conductivity is determined by the significant growth of the ions aggregation in corresponding solutions SBPBF4/AN.

Further, by using quantum theory "Atom in Molecules" analysis, the significant role of weak hydrogen bonds between fluorine atoms of the anion and hydrogen atoms of the methyl and methylene groups of the cation has been established [3].

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