

Microscopic Structure and Dynamics in mixture of Ionic Liquid and solvents : Molecular modelling and Spectroscopy Analysis

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Mixtures of imidazolium ionic liquids (ILs) with perfluorinated anions and polar aprotic solvents are promising candidates for electrolytic components used in different electrochemical devices. Current state of technologies requires detailed information on the influence of the nature of the constituents and of the mixture composition on the microscopic level structure and dynamics.

This contribution presents a molecular dynamics simulation analysis of the local structure organization of the mixtures of 1-butyl-3-methylimidazolium ($C4mim^+$) ILs with perfluorinated anions (BF_4^- , PF_6^- , TFO^- , $TFSI^-$) and dipolar aprotic solvents such as acetonitrile (AN), γ -butyrolactone (GBL) and propylene carbonate (PC).

As a first step, the local structure in the neat ILs and molecular solvents has been analyzed. For the set of ILs it was established that H-bonding interactions at the H^2 site is strongly enhanced compared to the H^{4-5} sites in the case of asymmetric and/or strongly basic anions like TFO^- or $TFSI^-$. The cation-cation contacts via the aggregation of the butyl chains is much stronger and less anion-dependent than the $\pi^+-\pi^+$ stacking of the imidazolium rings.

For the pure solvent our results show that although the dominant dipole-dipole orientation between a reference molecule and first neighbor is the antiparallel one, while for the subsequent neighbors the antiparallel orientation is gradually weakened in favor of the parallel one. More distant neighbors tend to be parallel to the reference molecule. A deep analysis of the local structure made it possible to identify the presence of weak hydrogen bonds in the selected dipolar solvents.

For the mixtures of imidazolium-based ILs the results show that in all the studied IL/molecular solvent mixtures, the distribution of the anion around the cation is not drastically affected in the range of x_{IL} between 1.00 and 0.30 and for further decrease of x_{IL} noticeable changes in the distance characteristics describing the cation and anion hydrogen bonding interactions, occur. These changes are associated with the expected weakening of the cation and anion interactions. These results are in good agreement with the behavior of the 2H chemical shift as a function of x_{IL} . Furthermore, our results point out to the importance of the anion-solvent interactions in describing the locale structure in these mixtures.