

Self-diffusion in the BmimPF₆/TfO - AN mixtures as seen by the quasi-elastic neutron scattering technique

Ya.I. Filatov^a, B.A. Marekha^{b,a}, A. Idrissi^b and O.N. Kalugin^a

^a *V.N. Karazin Kharkiv National University, School of Chemistry, Svoboda sq., 4. Kharkiv, Ukraine, E-mail: iaroslav647@gmail.com*

^b *University of Lille, Faculty of Sciences and Technologies, LASIR, Bât. C5, Cité Scientifique, 59655, Villeneuve d'Ascq Cedex, France*

Motivated by their potential use as electrolytes in electrochemical applications, the mixtures of 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆) and trifluoromethylsulfonate (BmimTfO), the commonly used ionic liquids (IL), with acetonitrile (AN) have been extensively studied by several experimental techniques in order to understand their macroscopic properties. Among the various direct experimental methods (i.e., those methods for which the space and time dimensions are comparable to the molecular dimensions and characteristic times of molecular processes, respectively), quasi-elastic neutron scattering (QENS) offers the most powerful techniques for analyzing ion and molecule dynamics in ionmolecular systems.

With the aim to elucidate the rotational and translational diffusive motions of Bmim⁺ cation in BmimPF₆ and BmimTfO ILs and their solutions in acetonitrile-D₃, QENS measurements were carried out as a function of a temperature and composition. We used the MANTID software package for the QENS data reduction and analysis in the framework of the Bulavin-Ivanov model.

According to the obtained results, translational and rotational diffusion can be characterized at quantitative level for all the samples apart from pure ILs. It was found out that in binary mixture with a molar fraction of ILs more than 1%, translational diffusion is provided by individual and collective contributions. The contribution of collective motion increases with increasing temperature and molar fraction of IL. The variation of translational diffusion as a function of temperature follows Arrhenius equation. As the molar fraction of ionic liquids in the analyzed binary solutions increases, the translational motion of Bmim⁺ cation slow down drastically and the activation energy of the process of translational diffusion of the cation increases several times, indicating a significant reinforcement of the inter-ionic association.