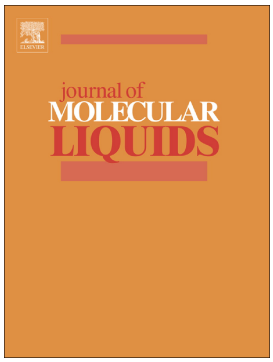

MD study of structure and dynamic properties of the 1-n-alkyl-3-methylimidazolium tris(perfluoroalkyl)trifluorophosphate ionic liquids

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MD study of structure and dynamic properties of the 1-n-Alkyl-3-Methylimidazolium tris(perfluoroalkyl)trifluorophosphate ionic liquids

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Abstract: In this study, we applied classical molecular dynamics (MD) simulations to understand the structure, dynamics and transport properties of the room-temperature 1-alkyl-3-methylimidazolium family with tris(perfluoroalkyl)trifluorophosphate ionic liquids, abbreviated as [$C_n$mim][eFAP]. Calculated densities of ionic liquids agree well with experimental data. Local structures were characterized by studying the center-of-mass (COM) and partial site-site RDFs, combined distribution functions (CDFs) and dihedral angles distribution of n-alkyl side chains in the imidazolium cations. The hydrogen bonding between Fluor atoms of anions and hydrogen atoms of imidazolium ring of cations were studied by contour maps of CDFs. Also, dynamical properties of these ILs such as mean-square displacement (MSDs) for center-of-mass of ions, ionic diffusion coefficients and the cationic transference numbers are calculated by simulation in the NVT ensemble. Results show that the length of alkyl-side chain of cation is the major factor to affect these properties.

Keywords: Fluorine. Ionic liquids. Molecular dynamics. Hydrogen bond. Dihedral angle

1. Introduction

During the last decade, ionic liquids (ILs) [1-5] have been the subject of considerable attention from researchers. Room-temperature ionic liquids (RTILs) are a class of ILs that are liquids at ambient room temperature. Their physicochemical properties can be tuned by combining a wide variety of cation and anion species. Some of their interesting physicochemical properties are low flammability, low volatility, low viscosity and high electrochemical stability [6]. For example, RTILs have been applied in various electrochemical devices (such as lithium secondary batteries and fuel cells), [7] tribology, [8] synthetic production, [9,10] and as biomass solvent [11,12]. Also, RTILs are so-called “designer solvents” owing to their semi-infinite chemical structures and combining of the different cations and anions [13]. RTILs also are a candidate for gas sorption, especially CO_2 as a green-house gas, and H_2S in the natural gas [14-16]. Imidazolium based ionic liquids are the most familiar ionic liquids in the last decade [17-20].

Hydrogen bonding between ions of RTILs and other species was the subject of many investigation in the last decade [21,22]. A wide number of experimental techniques, such as X-ray diffraction, mid-infrared and NMR spectroscopy was intensely studied [23-29] to probe the nature of hydrogen bonding in imidazolium based ionic liquids. Also, theoretical methods such as quantum chemistry calculations and classical molecular simulations [30] are performed on the systems containing a few ion pairs to detect the hydrogen bonding in these ionic liquids. Bonhôte et al., [31] observed that the methylation of the position C2 of 1-alkyl-3-methylimidazolium based ILs, and subsequently elimination of the C2–H2…X hydrogen bond leads to a liquid with higher viscosity and melting points, a somehow unexpected result (lower melting point and a decrease in viscosity would be expected) [32]. For example, Kirchner and co-workers [33] used ab initio molecular dynamics to illustrate a perspective on hydrogen bonds in the 1-ethyl-3-methylimidazolium acetate–water mixtures. However, there is still debated discussion on the effect of the hydrogen bond on the physicochemical properties in ionic liquids.

In this work we have studied the liquid structure, hydrogen bonding and Diffusion coefficient of 1-alkyl-3-methylimidazolium family with tris(perfluoroalkyl)trifluorophosphate, [$C_n$mim][eFAP], ionic liquids in detail by molecular dynamics simulations. ILs with fluorinated anions like [$C_n$mim][PF6] are hydrolytically unstable [34]. [$C_n$mim][eFAP] ionic liquids was first synthesized by

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