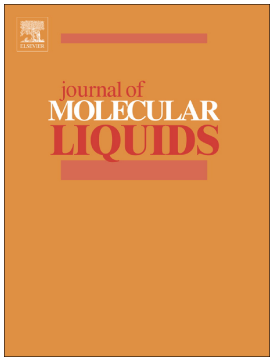

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Valérie Mazan, Maria Boltoeva

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Insight into the Ionic Interactions in Neat Ionic Liquids by Diffusion Ordered Spectroscopy Nuclear Magnetic Resonance

Valérie Mazan[a*] and Maria Boltoeva[a]

[a] Université de Strasbourg, CNRS, IPHC UMR 7178, F-67000 Strasbourg, France

*The corresponding author contact information: E-mail: valerie.mazan@iphc.cnrs.fr

Tel: +33 388 10 65 03

ABSTRACT

In this article, the transport properties of 1-alkyl-3-methylimidazolium [$C_n$mim$^+$] (n = 2, 4, 6, 8 and 10) or *N*-propyl-*N*-methylpyrrolidinium [C_3C_1pyrr$^+$] cations and *bis*(trifluoromethanesulfonyl)imide [Tf_2N^-] anions were studied by Diffusion Ordered Spectroscopy Nuclear Magnetic Resonance (DOSY NMR). The self-diffusion coefficients *D* of the cations and anions were measured. The values of *D* decrease in order [C_2mim][Tf_2N] > [C_4mim][Tf_2N] ≈ [C_3C_1pyrr][Tf_2N] > [C_6mim][Tf_2N] > [C_8mim][Tf_2N] > [C_{10}mim][Tf_2N]. For [$C_n$mim][Tf_2N] with n = 2, 4 and 6 and [C_3C_1pyrr][Tf_2N], the ionic liquid cation diffused faster than anion, for n = 8, the cation and anion diffused almost with the same speed and the cations and anions diffused together for n = 10. The motion of each ion of [$C_n$mim][Tf_2N] and [C_3C_1pyrr][Tf_2N] is connected with macroscopic physical properties such as viscosity, conductivity and microscopic aspects as intermolecular forces, local microstructure and dynamic heterogeneities of cations. Each coulombic force, hydrogen bonding and Van der Waals interactions play a role and the equilibrium between them is changed with the length of alkyl chain in the imidazolium-based ionic liquid.

Keywords

Ionic liquid, DOSY NMR, self-diffusion coefficient, ion pairing, hydrogen bonding

1. Introduction

Ionic Liquids (ILs) are a wide class of salts with melting point lower than 100°C and even part of them are liquid at room temperature. ILs consist entirely of ions, namely of asymmetric bulky organic cation and organic or inorganic anion. The cations used for the preparation of common and more investigated ILs are alkyl-substituted ammonium, phosphonium, imidazolium, pyridinium and pyrrolidinium [1]. Common anionic components of ILs are halides, hexafluorophosphate, tetrafluoroborate, tosylate, methanesulfonate and bis(trifluoromethanesulfonyl)imide. The physicochemical properties of ILs such as density, viscosity, miscibility with other solvents, etc. can be adjusted by appropriate choice of cationic and anionic part of IL. Ionic liquids possess attractive physicochemical properties, such as high chemical and thermal stability [2], non-flammability [3], very low vapour pressure [4, 5], etc. which make them a promising alternative to conventional organic