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Self-diffusion of phosphonium Bis(Salicylato)Borate ionic liquid in pores of Vycor porous glass



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ABSTRACT

 1H NMR pulsed field gradient was used to study self-diffusion of a phosphonium bis(salicylato)borate ionic liquid ([P_{6,6,6,14}][BScB]) in the pores of Vycor porous glass at 296 K. Confinement in pores increases diffusion coefficients of the ions by a factor of 35. However, some [P_{6,6,6,14}][BScB] ions demonstrated apparent diffusion coefficients much lower than their mean values, which may be due to partially restricted diffusion of the ions. We suggest that this fraction corresponds to areas where ions are confined by pore 'necks' (micropores) and empty voids. Heating of the ionic liquid/Vycor system at 330 K led to a change in the diffusivity of the ions, because of their redistribution in the pores. The size of the bounded regions is on the order of 1 μm , as estimated from the dependence of the ion diffusivity on the diffusion time.

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1. Introduction

Ionic liquids (ILs) are compounds composed of organic cations and organic or inorganic anions. They possess unique physical-chemical properties such as negligible vapor pressure, non-flammability, and high thermal and chemical stability. Hence, they represent an attractive material for modern industry applications. Recently synthesised halogen-free, boron-based ionic liquids (hf-BILs) composed of chelated orthoborate anions and phosphonium cations are hydrophobic and have high hydrolytic stability, low melting points and outstanding wear and friction-reducing properties [1]. The bulk physical properties of some of these ILs, such as diffusion, have demonstrated a tendency for micro-phase separation [2]. However, the properties of ILs at the liquid/surface interface and in confinement can be significantly different from those in bulk. Previously, a few groups reported on

* Corresponding author. E-mail address: Andrei.Filippov@ltu.se (A. Filippov). solid-like layers, which ions of ILs may form on solid surfaces and in confined spaces [3–5]. Experiments probing translational dynamics of ILs confined in pores demonstrated elevated mobility of different classes of ILs [5–10]. However, the physical properties of phosphonium-orthoborate ILs near surfaces and in restricted spaces have not yet been studied; nevertheless, they might be important to understand the lubrication performance of these ILs as well as properties of porous materials.

The purpose of this work was to study the bulk and confined self-diffusion of one of a series of ionic liquids that contains phosphonium cations [P_{6,6,6,14}]⁺ and the bis(salicylato)borate anion [BScB]⁻ and to demonstrate properties of the [P_{6,6,6,14}][BScB]⁻ ionic liquid as a promising neat lubricant or as an additive to traditional lubricants. For studies of the confined self-diffusion of this IL, a model mesoporous material, Vycor porous glass, was employed and the samples were probed using ¹H pulse-field-gradient (PFG) nuclear magnetic resonance (NMR) spectroscopy, an effective method to study the molecular diffusion of complex chemical substances [2.11.12].