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

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ABSTRACT

^{1}H 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.

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 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 ^{1}H pulse-field-gradient (PFG) nuclear magnetic resonance (NMR) spectroscopy, an effective method to study the molecular diffusion of complex chemical substances [2,11,12].

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2. Materials and methods

2.1. Materials

The studied ionic liquid contains trihexyltetradecylphosphonium cations, $[P_{6,6,6,14}]^+$, and bis(salicylato)borate anions, $[BScB]^-$. Molecular structures of the ions are shown in Fig. 1. $[P_{6,6,6,14}][BScB]$ was synthesised in the Chemistry of Interfaces of Luleå University of Technology and characterised and described previously by Shah et al.[1] $[P_{6,6,6,14}][BScB]$ is a transparent viscous liquid. Before introducing the IL into pores, it was degassed under vacuum (pressure less than 10^{-3} mbar and temperature 333 K) for 50 h. The chemical composition of the IL sample (content of IL and impurities) was checked by liquid ^1H, ^{13}C and ^{11}B NMR and has been described by Shah et al. [1].

Vycor 7930 porous glass was purchased from Advanced Glass & Ceramics (St. James, NC) [13,14]. Vycor has the form of a cylinder with a length of 15 mm and a diameter of 4 mm. It is characterised mainly by a 4-nm pore size, 28% volume open porosity and an internal surface area of *ca* 250 m^2 g^{-1}. Before use, the glass was cleaned by heating in a 30% hydrogen peroxide aqueous solution at 373 K for 48 h. Afterwards, it was washed with distilled water and dried under vacuum. Activation of the glass was performed at 473 K for 1 h. The glass cylinder was then cooled and placed in a bath with $[P_{6,6,6,14}][BScB]$ under vacuum, then atmospheric pressure was applied for two weeks at 294 K. After that, the sample was removed from the bath, wiped with filter paper and placed in a glass sample tube.

The sample was weighed and calculations taking into account the density of bulk $[P_{6,6,6,14}][BScB]$ (1.0193 g cm^{-3} at 293 K) showed that approximately 70% of the pores (~21% of the sample volume) were filled. We have estimated a filling factor of the same Vycor cylinder for water (H_2O) using bulk water density (0.997 g cm^{-3} at 293 K) and observed that 100% of the pores (~a factor of 0.29 of the Vycor cylinder volume) were filled. Taking this into account, the apparent value for the volume filling factor of 70% of IL in Vycor may reveal that: (i) the density of $[P_{6,6,6,14}][BScB]$ in pores is smaller to that in bulk; (ii) $[P_{6,6,6,14}][BScB]$ occupies only some areas of the pores; and (iii) both situations (i) and (ii) may occur. In the case of (ii), empty voids, which are not filled with the IL, may exist in the porous space.

Just after preparation, the sample was studied by NMR at 296 K, and then heated at 330 K for 3 h to homogenize the distribution of the IL inside the pores. The samples were then studied again by NMR at 296 K.

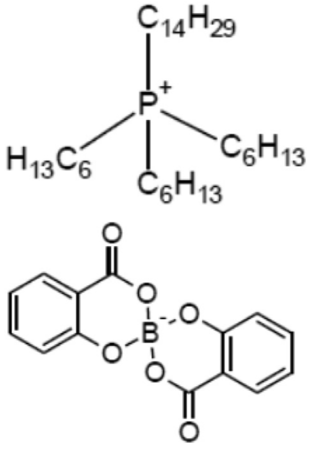

Fig. 1. Ionic components of the $[P_{6,6,6,14}][BScB]$ ionic liquid: The $[P_{6,6,6,14}]^+$ cation (top) and the $[BScB]^-$ anion (bottom).

2.2. Nuclear magnetic resonance

NMR measurements were performed on a Bruker Avance III (Bruker BioSpin AG, Fällanden, Switzerland) NMR spectrometer. The working frequency for ^1H was 400.27 MHz and 128.328 MHz for ^{11}B. Data were processed using Bruker Topspin 3.1 software. NMR self-diffusion measurements were performed on ^1H with a Pulsed-Field-Gradient (PFG) probe Diff50 (Bruker) with a maximum amplitude of the magnetic field gradient pulse of 30 T m^{-1}. The sample was placed in a standard 5-mm glass sample tube and closed with a plastic stopper to avoid contact with air. Before measurements were taken, the sample was equilibrated at 296 K for 1 h.

Details of the pulsed field gradient NMR technique used for measuring molecular diffusion can be found elsewhere [15]. Briefly, the primary information for the diffusion study by NMR is contained within the diffusion decay (DD) of the NMR spin-echo or stimulated echo amplitude. For the stimulated echo pulse sequence (Ste) used, the diffusion decay (*A*) can be described by equation (1) [15,16]:

$$A(2\tau, \tau_1, g, \delta) = \frac{I}{2}\exp\left(-\frac{2\tau}{T_2} - \frac{\tau_1}{T_1}\right)\exp\left(-\gamma^2\delta^2g^2Dt_d\right) \qquad (1)$$

where I is the factor proportional to the proton content in the system; T_1 and T_2 are spin-lattice and spin-spin relaxation times, respectively; τ and τ_1 are time intervals in the pulse sequence; γ is the gyromagnetic ratio for the measured nuclei; g and δ are the amplitude and duration of the gradient pulse; $t_d = (\Delta - \delta/3)$ is the diffusion time; $\Delta = (\tau + \tau_1)$ is the time interval between the two gradient pulses; and D is the self-diffusion coefficient.

Data reported here suggests that during the experimental diffusion time, molecules were displaced by distances far exceeding the pore sizes. Thus, being orthogonal to the pore walls, the molecules undergo all possible orientations of the internal magnetic field gradients. Hence, in the monopolar version of the pulse sequence, Ste, the internal gradients contribute with some "average" effect. However, to demonstrate the absence of any effect of the internal field gradient directly, a 13-interval stimulated echo sequence with bipolar gradient pulses [17] (Bp2) modified by including a longitudinal Eddy-current-delay [18] was also used. The latter pulse sequence removes cross-terms arising from the applied pulsed gradients, g and g_0, which are significant even if g_0 values are small. In our measurements, δ was 2 ms, τ was 5 ms (Ste) or 7.24 ms (Bp2), t_d was set in the range of 17–600 ms, and the amplitude of g was varied from 0 to 5 T m^{-1}.

3. Results and discussion

3.1. ^1H and ^{11}B NMR spectra in bulk and confined $[P_{6,6,6,14}][BScB]$

Fig. 2A–B shows the ^1H NMR spectra of $[P_{6,6,6,14}][BScB]$ in bulk and confined in pores of Vycor, respectively. ^1H chemical shifts for this IL have been reported by Shah et al. [1]. The range of 0.8–2.0 ppm corresponds to alkyl chains of the cation $[P_{6,6,6,14}]^+$, while the aromatic range of 6.5–8.2 ppm corresponds to the anion $[BScB]^-$ [1]. Resolution of the spectra is much poorer for the IL confined in pores (Fig. 2B), which may be the result of slower rotational mobility of the ions in the pores, resulting in insufficient averaging of the proton dipolar interactions. Nevertheless, signals from both the cation and anion still can be readily distinguished in the ^1H NMR spectrum. Therefore, the spectral lines can be used to