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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.

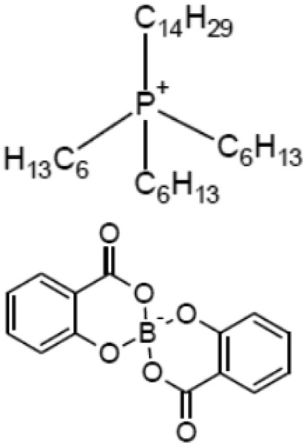

Fig. 1. Ionic components of the $[P_{6,6,6,14}][BScB]$ ionic liquid: The $[P_{6,6,6,14}]^+$ cation (top) and the $[BScB]^-$ anion (bottom).

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

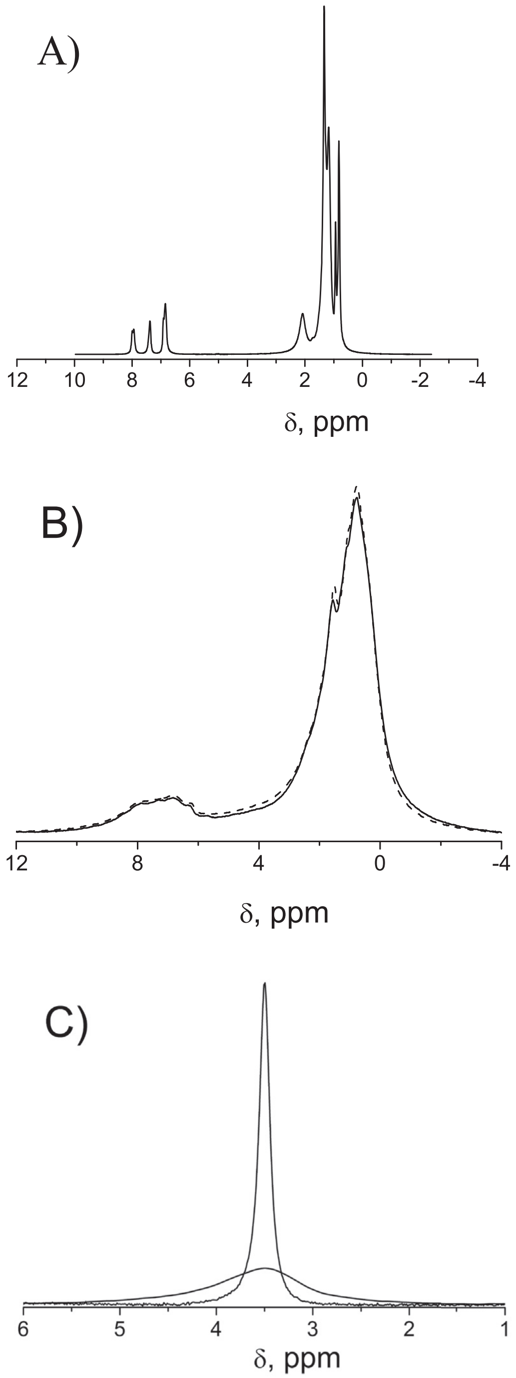

Fig. 2. ^{1}H NMR spectra of bulk [$P_{6,6,6,14}$][BScB] (**A**), and [$P_{6,6,6,14}$][BScB] in pores of Vycor before (solid line) and after heating at 330 K (dashed line) (**B**). ^{11}B NMR spectra of bulk [$P_{6,6,6,14}$][BScB] (narrow line) and [$P_{6,6,6,14}$][BScB] in pores of Vycor after heating at 330 K (broad line) (**C**). T = 296 K.

selectively measure diffusion decays corresponding to the cations or anions in the pores. Heating at 330 K for 3 h does not change the form of the ^{1}H NMR spectra for the IL in pores (solid and dashed lines in Fig. 2B). ^{11}B NMR spectra were also obtained for the sample before and after heating at 330 K for 3 h (see Fig. 2C), which revealed a broad resonance line (lw ≈ 1 ppm) at *ca* 3.5 ppm, i.e., the same shift as for the bulk [$P_{6,6,6,14}$][BScB] [1]. The significant line broadening in the ^{11}B NMR spectrum of [$P_{6,6,6,14}$][BScB] in pores probably occurs for the same reasons as the broadening of the resonance lines in the ^{1}H NMR spectra (Fig. 2B). Interestingly, confinement of [$P_{6,6,6,14}$][BScB] in pores does not change the ^{11}B chemical shift of the IL. It is known that the ^{11}B NMR chemical shift for orthoborate anions is very sensitive to the chemical structure of the anion [1]. For example, the boron site in the bis(mandelato) borate anion has a ^{11}B chemical shift of ~10.8 ppm, while for the bis(oxalato)borate anion it is ~7.3 ppm, for bis(malonato)borate it is ~3.4 ppm and for the [BScB]$^-$ anion it is ~3.5 ppm. The same value of the ^{11}B chemical shift of [BScB]$^-$ inside Vycor pores suggests chemical stability of the anion and a rather weak interaction with the surface sites of the Vycor glass. Even after heating at 330 K for 3 h, there was no change in the ^{11}B chemical shift and no additional resonance lines that could correspond to decomposition products of the [BScB]$^-$ anion.

3.2. *Diffusion of [$P_{6,6,6,14}$][BScB] in bulk*

Diffusion decays (DDs) for different ^{1}H NMR resonance lines of the bulk [$P_{6,6,6,14}$][BScB] in ^{1}H PFG NMR experiments are all single-component decays for both the cation and anion, but the slopes of the decays are different (Fig. 3). The diffusion coefficient of the [BScB]$^-$ anion estimated from these DDs is ~16% larger than that of the [$P_{6,6,6,14}$]$^+$ cation, which means that the cation and anion diffuse separately, at least to some extent.

3.3. *Experimental results of diffusion of [$P_{6,6,6,14}$][BScB] in pores of Vycor*

3.3.1. *Before heating at 330 K*

Diffusion decays for both types of ions of [$P_{6,6,6,14}$][BScB] in pores strongly depend on the diffusion time. Fig. 4A–C show DDs at diffusion times of 17, 170 and 300 ms, respectively. In these figures, one can see that the DDs of [$P_{6,6,6,14}$][BScB] in pores have rather complicated forms. The analysis showed that each of the decays (for the cation and the anion) is close to a two-exponential decay. The analysis of the diffusion coefficients of the components was mostly straightforward for DDs obtained at a shorter diffusion time, 17 ms, (Fig. 4A, Table S1 in the ESI). Diffusion coefficients (Ds) corresponding to the "faster" diffusion components for cations and anions are roughly a factor of 35–40 larger than those of the "slower"

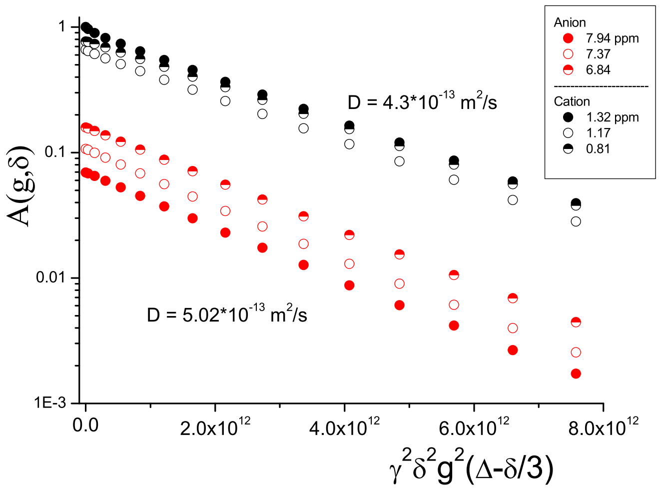

Fig. 3. Diffusion decays of ^{1}H NMR spectra signals corresponding to the [BScB]$^-$ anion (red) and the [$P_{6,6,6,14}$]$^+$ cation (black) of [$P_{6,6,6,14}$][BScB] in bulk at 296 K. Mean diffusion coefficient values for the cation and anion are shown near the decays. DDs are normalised to the amplitude of the cation signal corresponding to 1.32 ppm at g = 0. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

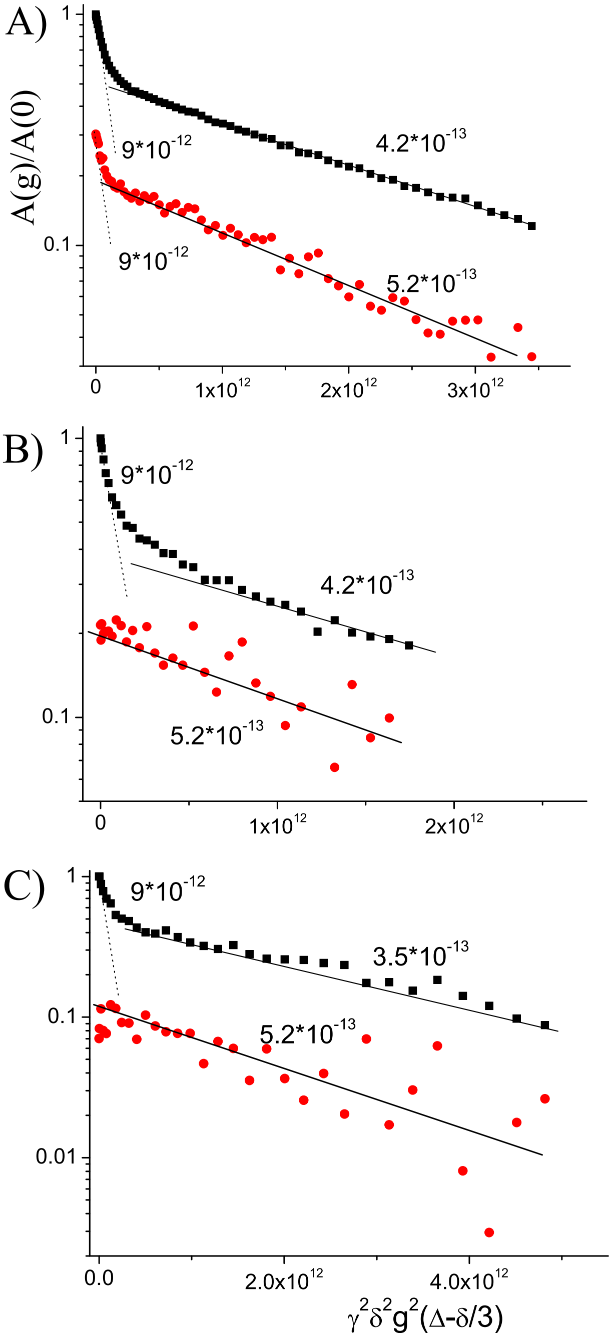

Fig. 4. Diffusion decays of ^{1}H NMR signals corresponding to the anion $[BScB]^-$ (red) and the cation $[P_{6,6,6,14}]^+$ (black) of $[P_{6,6,6,14}][BScB]$ in pores of Vycor before heating at 330 K. Diffusion times: 17 ms (**A**), 170 ms (**B**) and 300 ms (**C**). T = 296 K. DDs are normalised to the signal of the cation at $g = 0$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

diffusion components. The latter are similar to Ds of cations and anions, respectively, in the bulk IL (compare with data in Fig. 3). Mean values of Ds calculated from the initial slopes of DDs for the cation and anion (dotted lines) are both close to $9 \cdot 10^{-12}$ m^2/s. Signals from the $[BScB]^-$ anion are noisier than those of the $[P_{6,6,6,14}]^+$ cation, because of the accelerated T_2 relaxation for the more rigid structure of the anion. As the diffusion time (and τ_1) increases, the signals from both anions and cations decrease, because of T_1 relaxation processes. Therefore, signals from the ionic liquid become noisier, particularly in the case of the $[BScB]^-$ anion. An increase in the diffusion time to 170 ms and further to 300 ms leads to the "faster" diffusion component of the anion disappearing under these experimental conditions (see Fig. 4B–C) due to NMR T_1 relaxation weighting. Mean Ds of the cation do not change under these experimental conditions but the apparent fraction of the "slower" component decreases, as shown in Fig. S1 in the ESI. Diffusion decays obtained using the stimulated echo pulse sequence with bipolar gradients (Fig. S1 of ESI) show essentially no significant effect of the bipolar gradient on the observed diffusion coefficients of the cation.

3.3.2. After heating at 330 K for 3 h

After heating the samples at 330 K for 3 h, there was also no difference in the results of the stimulated spin echo with monopolar and bipolar pulsed field gradients compared to the data obtained for the unheated samples. An example demonstrating this is shown in Fig. S2 of the ESI. However, after heating the sample, diffusion decays changed significantly (Fig. S3 of ESI). DDs also changed with an increase in diffusion time as shown in Fig. 5. For the diffusion time of 17 ms (Fig. 5A), DDs can only roughly be described as sums of two components (Table S1 in the ESI) and the values of slower diffusion coefficients increase relative to the sample before heating (Fig. 4A); diffusion coefficients of slow-diffusing components increase by *ca* 10-fold compared to the unheated sample described above. For the 300-ms diffusion time (Fig. 5B), the apparent fraction of the "slowly" diffusing component assigned to the cation decreases (from ~0.32 to ~ 0.25), while the DD for the anion demonstrates almost single-component diffusion. Finally, for the 600-ms diffusion time (Fig. 5C), DDs for both the cation and anion appear nearly identical to those of single-component diffusion. A comparison of DDs for the cation $[P_{6,6,6,14}]^+$ is also shown in Fig. S4 of the ESI.

The DDs for the cation and anion change, while mean values of Ds of both ions ($9 \cdot 10^{-12}$ m^2/s) are almost independent of the diffusion time in the entire range of diffusion times studied. Such behavior is typical for the process of exchange between states with different Ds if the lifetimes of the molecules in these states are in the time-scale of the diffusion measurements [11,12].

All diffusion coefficients obtained by two-exponential approximations are summarised in Fig. 6 and in Table S1 in the ESI.

3.4. Diffusion of $[BScB]^-$ and $[P_{6,6,6,14}]^+$ ions in pores of Vycor

Enhanced diffusion of fluids has been observed previously in porous and dispersed fluids. A "gas-like" state of water and liquid hydrocarbons has been revealed in partially filled dispersed and porous systems [19], which has been explained by the presence of saturated gas phase in equilibrium with water under conditions of fast exchange in the time scale of the NMR diffusion experiment. For fully filled pores of Vycor porous glass, the effect was different for hydrocarbons and water: effective diffusion of hydrocarbon decreases, while relative diffusivity of water increases; that has been explained by destruction (at least, partial) of hydrogen bonds presenting in bulk water [11]. Concerning ionic liquids, enhanced diffusivity of *N*,*N*,*N′*,*N′*-tetramethylguanidinium bis(perfluoroethylsulfonyl)imide ($[H_2NC(dma)_2][BETI]$) in ordered mesoporous carbon (pore diameter ~ 8.8 ± 2.1 nm) has been observed by Chathoth et al. [7,8]. Rachocki et al. [20] studied indirectly, by means of fast field-cycling ^{1}H NMR relaxometry, the translational diffusion of cations in a gel polymer electrolyte based on ethoxylated bisphenol dimethacrylate and *1*-butyl-*3*-methylimidazolium tetrafluoroborate ($[BMIm][BF_4]$). It was found that the diffusion coefficient of the cation is a factor of 2–3 higher than that of cations in pure IL. For the same IL confined in porous silicon membranes with pore sizes of 7.5–10.4 nm, Iacob et al. [10] reported about two

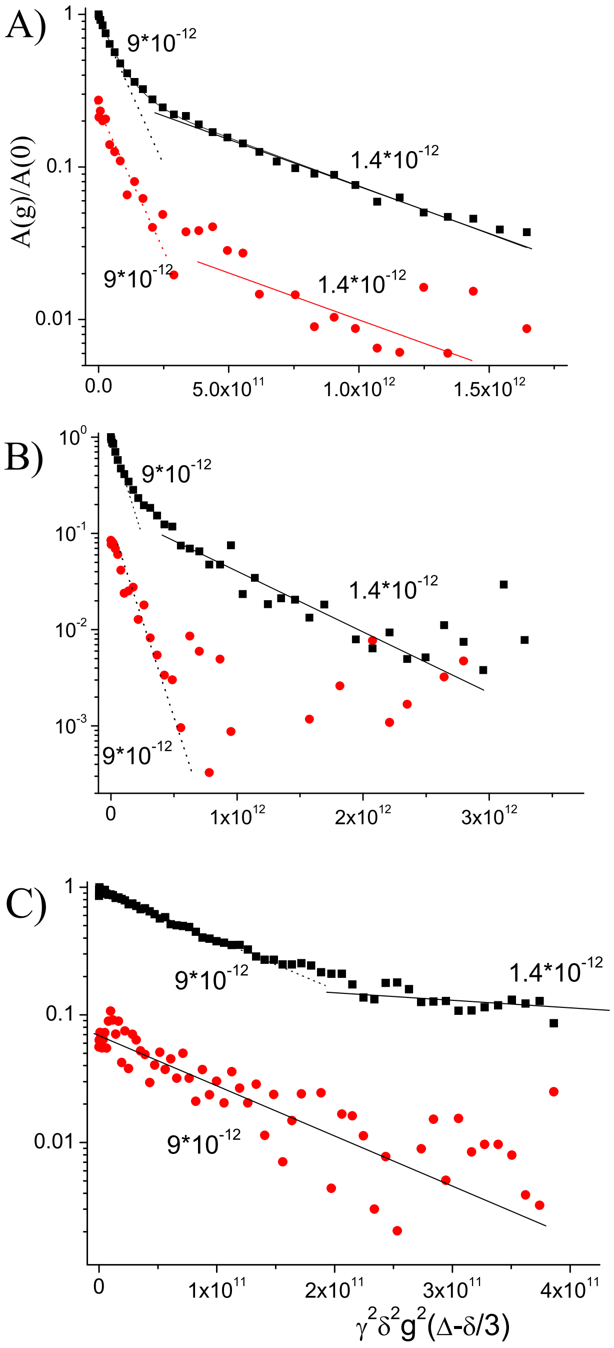

Fig. 5. Diffusion decays of ^{1}H NMR signals corresponding to the anion $[\mathrm{BScB}]^-$ (red) and the cation $[\mathrm{P}_{6,6,6,14}]^+$ (black) of $[\mathrm{P}_{6,6,6,14}][\mathrm{BScB}]$ in pores of Vycor after heating at 330 K. Diffusion times: 17 ms **A**), 300 ms **B**) and 600 ms **C**). T = 296 K. DDs are normalised to the signal of the cation at $g = 0$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

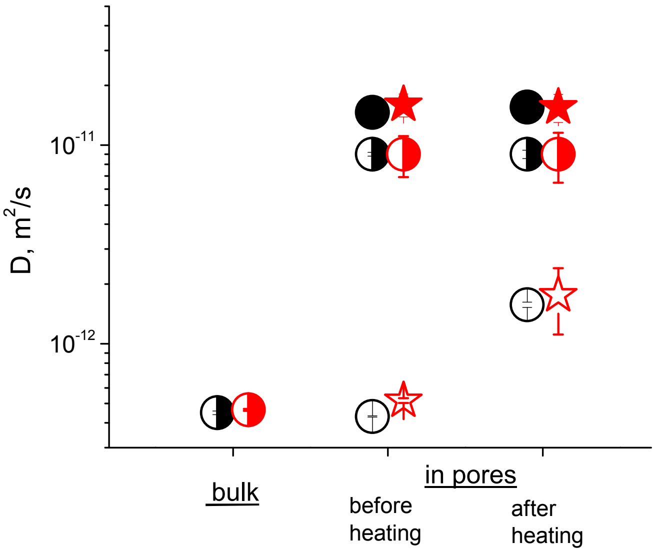

Fig. 6. Diffusion coefficients of $[\mathrm{P}_{6,6,6,14}]^+$ (black) and $[\mathrm{BScB}]^-$ (red) in bulk and in pores of Vycor. Half-filled circles correspond to mean values, filled circles to "fast" fractions and open circles to "slow" fractions. T = 296 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

orders of enhancement of self-diffusion. In our study, the mean values of the diffusion coefficient of $[\mathrm{P}_{6,6,6,14}][\mathrm{BScB}]$ ions in pores of Vycor are also about a factor of 35–40 larger than those in bulk (Figs. 4 and 5). This observation extends the number of ILs for which this effect takes place. Therefore, enhanced diffusion in confinement is relevant to associated fluids, like water and some ILs.

Mechanisms leading to the enhancement of diffusion of ILs in pores have been discussed. Chathoth et al. have suggested that the effect might be the result of structural changes of the IL within the pores whereby IL forms a layered structure near the pore wall [8]. The enhancement of diffusivities by more than two orders of magnitude has been attributed by Iacob et al. to changes in molecular packing density leading to higher mobility; theoretical studies of spherical balls in cylindrical containers indicate that the mass density decreases by up to 7% when the radii of the balls become comparable to that of the confining cylinder [10]. This agrees with atomistic simulations of Shi and Sorescu [21], who studied diffusion in $[\mathrm{HMIm}][\mathrm{NTf}_2]$ confined in 4.5-nm-diameter carbon nanotubes and observed a decrease in the mass density compared to the bulk value, leading to an increase of the diffusion coefficients by about two orders of magnitude. Generally, all of these arguments agree with our observation of enhanced diffusivity and decreased apparent density of the $[\mathrm{P}_{6,6,6,14}][\mathrm{BScB}]$ in pores of Vycor.

Nevertheless, in discussions of the elevated diffusion coefficients for fluids in pores, much less attention has been paid to the distribution of apparent diffusivities, which manifests, particularly, in complex forms of NMR diffusion decays. A single diffusion coefficient and independence of Ds on diffusion time (3–1000 ms) have been observed for liquid hydrocarbons confined in Vycor at 303 K [11], which demonstrated complete averaging of diffusivity when fast molecular exchange occurs between different ranges of pores. No such results have been reported for $[\mathrm{BMIm}][\mathrm{BF}_4]$ in porous silicon membranes [10]. However, for $[\mathrm{H}_2\mathrm{NC(dma)}_2][\mathrm{BETI}]$ in mesoporous carbon [8] and for $[\mathrm{P}_{6,6,6,14}][\mathrm{BScB}]$ in pores of Vycor (our data), a component has been reported to have slower diffusion relative to the main component. The "slow diffusion coefficients" for $[\mathrm{P}_{6,6,6,14}][\mathrm{BScB}]$ are a factor of 10–40 smaller than those of the "fast diffusion coefficients" (Figs. 4 and 5). Chathoth et al. [8] recently mentioned the second diffusion coefficient, but provided no suggestions about its nature, probably because of the absence of details about the porous structure of carbon. In our case, the structure of Vycor has been characterised in a number of absorption studies; this allows us to offer suggestions about the nature of the slower component of diffusivity.

The pore space of Vycor is formed by a process of spinodal decomposition of a boron-rich phase, which is then chemically etched out, resulting in a random, interconnected pore space

[13,14,17]. The mean pore diameter is ~4 nm. Pore size distributions of Vycor have been obtained previously by different techniques: nitrogen adsorption, mercury intrusion and small-angle scattering, as reported by Gille et al. [22], and by SAXS in the paper by Mitropoulis [23]. All distributions demonstrated an essential fraction of the pores with diameters less than 1 nm. A recent adsorption-desorption and Monte Carlo study by Cimino et al. [24] showed that Vycor has a highly disordered silica matrix with a network of pores containing alternating enlargements (voids) and constrictions ('necks') that determine the diffusion properties of Vycor. Our estimation, based on the chemical structure, reveals the approximate sizes of $[P_{6,6,6,14}]^+$ as 0.35 × 0.35 × 2.56 nm and $[BScB]^-$ as 0.38 × 0.41 × 1.21 nm, which are both less than the mean pore diameter in Vycor. However, diffusion of these ions through pores with diameters less than ~0.35 nm is effectively stopped. The fraction of such pores ('necks') estimated from the distribution function obtained by Cimino et al. [24] is nearly 0.4. We suggest that the presence of such pore 'necks' in Vycor is the main type of barrier that leads to the observation of a fraction of slowly diffusing $[P_{6,6,6,14}][BScB]$ in Vycor pores.

The second possible type of barrier for diffusion of IL in Vycor may be small, randomly distributed empty voids with an average radius of ~5 nm, consistent with possible areas where the pores intersect [17]. Indeed, the apparent filling factor of the pores by this IL, ~70%, cannot be explained only by the lower density of the IL (for example, a reduction in density is only about 7% in the case of $[BMIm][BF_4]$ in porous silicon membranes [10]). Therefore, Vycor glass filled with $[P_{6,6,6,14}][BScB]$ should contain some fraction of empty voids.

The observation of two components with different diffusion coefficients indicates the presence of two dynamic phases of $[P_{6,6,6,14}][BScB]$. Diffusion-time dependences of DDs show the typical effects of exchange between dynamic phases with different Ds [12]—maintenance of the mean diffusion coefficient estimated from the initial slope of the diffusion decay (see Figs. 4 and 5 for the cation, and Figs. 4A and 5 for the anion) and a decrease in the apparent fraction of the "slow-diffusion" component. Based on this consideration, we can suggest that the fraction of $[P_{6,6,6,14}][BScB]$ represented by the "slow diffusion coefficient" is confined in certain volumes ("partially isolated volumes") inside Vycor pores that are separated by micropores of the Vycor and/or by empty voids. From the diffusion time dependences (Figs. 4 and 5), it can be concluded that the "partially isolated volumes" of $[P_{6,6,6,14}][BScB]$ exchange ions through the network of pores in different regimes of the exchange of molecules (ions) [12]. Those are determined by ratios between the lifetime of a molecule (ion) in a state characterised by "fast" or "slow" diffusion coefficients and the diffusion time (t_d) of the NMR diffusion experiment. For $[P_{6,6,6,14}]^+$ in the sample before heating and in the range of diffusion times from 17 to 300 ms, there is a "slow exchange" regime where DD maintains its complex form in the entire range of t_d. For $[BScB]^-$, the "fast diffusion coefficient" is observed only at 17 ms, but disappears at longer diffusion times, most probably because of the short T_1 NMR relaxation of $[BScB]^-$ protons due to absorption in the micropores. The "slow diffusion coefficient" of the anion is comparable with that of the cation in the whole range of 17–170 ms (Fig. 4A–B) and corresponds to diffusion in "partially isolated volumes" of pores. Thus, the anion also diffuses in pores in the "slow exchange" regime. After heating at 330 K, redistribution of the IL leads to a change of the diffusion regime. Now the DD for $[P_{6,6,6,14}]^+$ and $[BScB]^-$ continuously changes from two-exponential (Fig. 5A) to single-exponential (Fig. 5B–C), so the cation and anion diffuse in pores between different volumes in the "intermediate exchange" regime. Therefore, redistribution of the IL as a result of heating facilitates exchange conditions for the cation and the anion.

The time scale of the averaging of diffusion is evident from the experimental DDs, but we can also estimate spatial scales of "partially isolated volumes", which are characterised by slow diffusion, using Einstein's relation for the mean-squared displacement:

$$\left(<r^2>\right)^{0.5} = (2 \cdot D_s \cdot t_d)^{0.5} \tag{2}$$

For the cation in the sample before heating ($Ds \sim 4.2 \cdot 10^{-13}$ m^2/s, maximal $t_d = 300$ ms), displacement in these volumes is less than 0.5 μm. No averaging occurs on this scale. After heating, Ds is ~$1.7 \cdot 10^{-12}$ m^2/s at averaging t_d ~300 ms, therefore displacement, which is effective for the averaging of diffusion in these volumes, is approximately 1 μm.

Confinement in pores of Vycor may result in at least two types of effects for ions: (i) interaction of ions with silica surfaces, and (ii) confinement of the IL in cylinders with diameters of nearly 4 nm. For the hydrophobic $[P_{6,6,6,14}]^+$ ion, the interaction with a hydrophilic silica surface may be a short-range and attractive interaction. Otherwise, the $[BScB]^-$ anion, with its oxygen groups, has a structure that resembles the catechol molecule [25,26]. Catechol strongly adheres to silica surfaces by forming hydrogen bonds with a hydroxyl and a phenylene ring, contributing to its adhesion [26]. These bonds are reversible [25], therefore they may fluctuate and adhesion may not stop the diffusion process. The difference between catechol and $[BScB]^-$ is that catechol is a flat and a neutral molecule, while $[BScB]^-$ is bulky and negatively charged, therefore, the energy of interaction of the $[BScB]^-$ anion with silica surfaces, which also carry a negative charge, should be lower and, thus, the lifetime of its hydrogen bonding with silica surfaces should be shorter compared to that of catechol molecules. On the other hand, the interaction between highly hydrophilic silica surfaces and $[BScB]^-$ anions is suggested to be stronger than the interaction between silica surfaces and highly hydrophobic $[P_{6,6,6,14}]$ cations, despite attractive electrostatic interactions between cations and silica surfaces. These arguments may be invoked to explain the decrease in the anion signal in connected thin pores, "partially isolated volumes", for a sample before heating (Fig. 4B–C).

Some ILs are prone to forming microstructures as a result of microphase separation in a certain range of temperatures due to competition of electrostatic and "hydrophobic" interactions [27–30], which has been confirmed by NMR diffusion measurements [31]. We suggest that confinement of an IL in pores, resulting in introducing additional interactions of ions with pores and restricting microphase volumes, may lead to modification or complete destruction of the microphase structure present in the bulk IL.

One observation of our study is that the heating does not have an effect on either the chemical shifts or broadening of the ^{1}H and ^{11}B NMR spectra, therefore, one can conclude that no cation or anion decomposition occurs upon heating of this sample. However, diffusion is different for the sample before and after heating at 330 K for 3 h. Evidently, the higher mobility of ions at 330 K allows them to redistribute in the porous space of Vycor in a more energetically favorable way, to reach equilibrium. Thus, DDs represent the characteristics of IL distribution in Vycor pores. Indeed, the pore space of the porous Vycor glass is continuous [32], therefore pores may be saturated with a fluid if pressure is applied. However, restricted connectivity of the pore space of Vycor is due to the presence of the pore 'necks' (micropores). At 294 K, the thermal energy is not enough to overcome this barrier ('neck'), which might be one of the reasons why the pores saturated with a fluid cannot reach equilibrium. However, heating to 330 K gives the ions extra energy to overcome this barrier and leads to redistribution of the IL and the empty voids in the sample.

4. Conclusions

^{1}H NMR pulsed field gradient was applied 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 enormously increases the diffusion coefficients of ions, by almost a factor of 35, however, some fraction of the ionic liquid demonstrated apparent diffusion coefficients by a factor of 10–40 lower than its mean value. We explained the appearance of this fraction by the presence of “partially isolated volumes” containing [$P_{6,6,6,14}$][BScB] in the Vycor pores, which is in a so-called “slow exchange” regime with the rest of the IL. Barriers separating “partially isolated volumes” from other areas of pores with IL may be due to micropores and/or empty voids in the Vycor glass. Heating of the IL/Vycor system at 330 K led to redistribution of [$P_{6,6,6,14}$][BScB] such that a “slow exchange” regime of diffusion is changed to an “intermediate exchange” regime. The size of “partially isolated volumes”, as estimated from the dependence of ion diffusivity on the diffusion time, is on the order of 1 μm. This study provides additional evidence of the existence of bulk microstructures in phosphonium orthoborate ionic liquids and modification of these microstructures near silica surfaces and in complex confinements. Microstructures of ILs near surfaces of different materials may influence the lubrication properties of these ionic liquids and IL performance in other applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2016.04.044.

References

[1] F.U. Shah, S. Glavatskih, D.R. MacFarlane, A. Somers, M. Forsyth, O.N. Antzutkin, Phys. Chem. Chem. Phys. 13 (2011) 12865–12873.

[2] A. Filippov, F.U. Shah, M. Taher, S. Glavatskih, O.N. Antzutkin, Phys. Chem. Chem. Phys. 15 (2013) 9281–9287.

[3] S. Bovio, A. Podesta, C. Lenardi, P. Milani, J. Phys. Chem. B 113 (2009) 6600–6603.

[4] L.A. Jurado, H. Kim, A. Arcifa, A. Rossi, C. Leal, N.D. Spencer, Phys. Chem. Chem. Phys. 17 (2015) 13613–13624.

[5] M.P. Singh, R.K. Singh, S. Chandra, Progr. Mater. Sci. 64 (2014) 73–120.

[6] T. Echelmeyer, H.W. Meyer, L.V. Wullen, Chem. Mater. 21 (2009) 2280–2285.

[7] S.M. Chathoth, E. Mamontov, S. Dai, X. Wang, P.F. Fulvio, D.J. Wesolowski, Europhys. Lett. 97 (2012) 66004.

[8] S.M. Chathoth, E. Mamontov, P.F. Fulvio, X. Wang, G.A. Baker, S. Dai, D.J. Wesolowski, Europhys. Lett. 102 (2013) 16004.

[9] C. Iacob, J.R. Sangoro, P. Papadopoulus, T. Schubert, S. Naumov, R. Valiullin, J. Kärger, F. Kremer, Phys. Chem. Chem. Phys. 12 (2010) 13798–13803.

[10] C. Iacob, J.R. Sangoro, W.K. Kipnusu, R. Valiullin, J. Kärger, F. Kremer, Soft Matter 8 (2012) 289–293.

[11] V. Skirda, A. Filippov, A. Sagidullin, A. Mutina, R. Archipov, G. Pimenov, Fluid Transport in Nanoporous Materials, in: Book Series: NATO Science Series II-mathematics Physics and Chemistry, vol. 219, 2006, pp. 255–278.

[12] J. Kärger, H. Pfeifer, W. Heink, Principles and Application of Self-diffusion Measurements by Nuclear Magnetic Resonance, vol. 12, Academic Press, New York, 1988, pp. 1–89.

[13] P. Levitz, G. Ehret, S.K. Sinha, J.M. Drake, J. Chem. Phys. 95 (1991) 6151–6161.

[14] Corning Glass Works, O. E. M. Sales Service, Box 5000, Corning, NY 14830.

[15] P.T. Callaghan, Principles of Nuclear Magnetic Resonance Microscopy, Clarendon, Oxford, 1991, p. 492.

[16] J.E. Tanner, J. Chem. Phys. 52 (1970) 2523–2526.

[17] R.M. Cotts, M.J.R. Hoch, T. Sun, J.T. Markert, J. Magn. Reson. 83 (1989) 252–256.

[18] S.J. Gibbs, C.S. Johnson Jr., J. Magn. Reson. 93 (1991) 395–402.

[19] N.K. Dvoyashkin, A.I. Maklakov, Colloid J. 58 (1996) 561–565.

[20] A. Rachocki, E. Andrzejewska, A. Dembna, J. Tritt-Goc, Eur. Polym. J. 71 (2015) 210–220.

[21] W. Shi, D.C. Sorescu, J. Phys. Chem. B 114 (2010) 15029–15041.

[22] W. Gille, D. Enke, F. Janowski, J. Porous Mater. 9 (2002) 221–230.

[23] A.C. Mitropoulos, J. Colloid Interface Sci. 336 (2009) 679–690.

[24] R. Cimino, K.A. Cychosz, M. Tommers, A.V. Neimark, Colloids Surf. A Physicochem. Eng. Asp. 437 (2013) 76–89.

[25] S.A. Mian, L.M. Yang, L.C. Saha, E. Ahmed, M. Ajmal, E. Ganz, Langmuir 30 (2014) 6906–6914.

[26] S.A. Mian, L.M. Yang, L.C. Saha, J. Jang, L. Wang, X. Gao, S. Nagase, J. Phys. Chem. 114 (2010) 20793–20800.

[27] T.L. Greaves, C.J. Drummond, Chem. Rev. 108 (2008) 206–237.

[28] G.L. Burrell, I.M. Burgar, Q. Gong, N.F. Dunlop, F. Separovic, J. Phys. Chem. B 114 (2010) 11436–11443.

[29] O. Russina, A. Triolo, L. Gontrani, R. Caminiti, Phys. Chem. Lett. 3 (2011) 27–33.

[30] K. Shimizu, M.F.C. Gomes, A.A.H. Padua, L.P.N. Rebelo, J.N.C. Lopes, J. Mol. Str. 946 (2010) 70–76.

[31] A.E. Frise, T. Ichikawa, M. Yoshio, H. Ohno, S.V. Dvinskikh, T. Kato, I. Furo, Chem. Commun. 46 (2010) 728–730.

[32] D.P. Bentz, E.J. Garboczi, D.A. Quenard Model, Simul. Mater. Sci. Eng. 6 (1998) 211–236.