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Suppression of the Anomalous Relationship between Diffusivities of Cations and Anions by Water in Imidazolium-Based Ionic Liquids

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Abstract

Proton pulsed field gradient (PFG) NMR technique at high magnetic field (17.6 T) and high magnetic field gradients (up to 30 T/m) is applied to study diffusion of the anions and cations in the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ([Emim][ETSO4]) with and without water. Excellent NMR spectral resolution attained by this technique allowed high-precision monitoring of the diffusivities of the anions, cations and water in a single experiment. The PFG NMR data show that the anomalous relationship between the ion diffusivities, *i.e.* larger self-diffusion coefficient of the bulkier [Emim] cation than that of the less bulky [ETSO4] anion, becomes much less pronounced due to addition of water into the ionic liquid. This observation is explained by the distortion of the local structure in the ionic liquid by water molecules leading to a possible loss of the diffusion anisotropy for the cation diffusion. The reported experimental data are in a qualitative agreement with the most recent results of molecular dynamics simulations (see references 9 and 10).

Introduction

Room temperature ionic liquids (RTILs) [1, 2] are salts that are liquid at ambient temperatures. They have negligible vapour pressure and represent environmentally safe and non-corrosive media. Many unique properties of RTILs have raised increasing interest in their applications as new media for organic synthesis, catalytic reactions, separation processes, and extraction. Translational diffusion of ions plays a large role in many of these applications. One of the most intriguing observations related to diffusion in RTILs is that a more bulky cation often diffuses faster than a less bulky anion. Such results were obtained for imidazolium-based ionic liquids by pulsed field gradient (PFG) NMR technique [3-5] as well as by molecular dynamics (MD) simulations [6-10]. In this letter we report PFG NMR experimental data showing that an addition of a small amount of water to an imidazolium-based RTIL can lead to a significant reduction and even disappearance of this anomalous relationship between the diffusivities of cations and anions. Due to hygroscopic nature of RTILs they can adsorb significant amounts of water from the surrounding atmosphere [11-14]. Hence, it is of great interest to develop fundamental understanding of an influence of water on diffusion properties of RTILs.

Pulsed field gradient (PFG) NMR [15-17] is ideally suited for investigations of ion diffusion in ionic liquids [3, 4, 18-22]. In contrast to many previously reported PFG NMR investigations of RTILs, in the present study the diffusion data for cations and anions were obtained simultaneously, *i.e.* in a single experiment, using proton PFG NMR. Such measurements were possible due to a combination [23, 24] of a high magnetic field (17.6 T) NMR allowing for the recording of NMR lines with an excellent spectral resolution and high (up to 30 T/m) magnetic field gradients, which were much larger than any susceptibility-induced inhomogeneities in the local magnetic field.

Experimental Section

The proton PFG NMR diffusion measurements were performed with the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ([Emim][ETSO4]) consisting of 1-ethyl-3-methylimidazolium ($[\mathrm{Emim}]^+$) cations and ethylsulfate ($[\mathrm{ETSO4}]^-$) anions. The ionic liquid samples with and without water were prepared in the group of Professor Joan F. Brennecke, University of Notre Dame, USA as described in ref. [25]. The water concentration in the studied samples of [Emim][ETSO4] was varied in the range between 0 and 15% w/w.

A wide-bore Bruker BioSpin NMR spectrometer operating at a proton resonance frequency of 750 MHz was used. Magnetic field gradients were generated using diff60 diffusion probe (Bruker BioSpin) and Great60 gradient amplifier (Bruker BioSpin). Diffusion measurements of ions and water were carried out using the standard PFG NMR stimulated echo pulse sequence [15-17]. In most cases it was sufficient to use gradients with the maximum amplitude of around 10 T/m.

Diffusion data were obtained from dependencies of the intensity of the PFG NMR signal (A) on the amplitude of the magnetic field gradients (g). The signal intensity was determined by integrating the area under selected line(s) of the frequency-domain NMR spectra recorded by the PFG NMR stimulated echo pulse sequence. Different lines in such spectra can correspond to different species. Hence, diffusion data for a chosen type of species in a sample can be obtained by selecting an appropriate line in the spectrum for data processing. For the NMR lines of ions exhibiting no significant overlap with the lines of other type of ions and/or water the diffusivity (D) was determined from the measured attenuation of the PFG NMR signal $\left(\Psi \equiv \frac{A(g)}{A(g=0)}\right)$ corresponding to this line using [15-17]

$$\Psi = \exp\left(-(\gamma\delta g)^2 D t_{eff}\right), \tag{1}$$

where γ is the gyromagnetic ratio, δ denotes the effective duration for rectangular gradient pulses, g is the amplitude of the magnetic gradients, t_{eff} is the effective diffusion time ($t_{eff} = (\Delta - \delta/3)$) , and Δ is the separation between the gradient pulses. In the studied samples the NMR line of water showed an overlap with the lines corresponding to either anion, cation or both. As a result, the attenuation curves for the water line containing some contribution from the ion signal were described as a sum of two or three weighted exponential terms of the type shown in Eq.1

$$\Psi = \sum_{i=1}^{n=2 or 3} A_i \exp\left(-(\gamma\delta g)^2 D_i t_{eff}\right), \tag{2}$$

where A_i and D_i represent the fraction and diffusivity of species i, respectively, and n is the number of different species contributing to the NMR line. The water diffusivity was determined from fitting the attenuation curves by Eq.2, which contained the known diffusivity(ies) of the anion and/or cation. The latter diffusivities were determined by Eq.1 using the corresponding "pure" NMR lines of the ions showing no overlap with the lines of other types of species. The existence of a contribution of the anion and/or cation line(s) to the water line was determined by analyzing the shape of the recorded NMR spectra.

The signal attenuation was measured under the conditions when only the value of g was varied and all other parameters in the PFG NMR stimulated echo sequence remained constant. The value of δ was in all cases much smaller than Δ, thus $t_{eff} \approx \Delta$. The effective diffusion time was changed by changing the value of Δ. The PFG NMR diffusion measurements were performed for at least two effective diffusion times equal to 24.8 ms and 49.8 ms and for two values of the time interval between the first and the second $\pi/2$ pulses of the PFG NMR stimulated echo sequence (τ) equal to 1.5 ms and 3.0 ms. For each temperature and water concentration the measured ion diffusivities at different values of t_{eff} and τ remained the same within the uncertainty less than ±10%. This uncertainty was used as an experimental uncertainty for ion diffusivities. The experimental uncertainty for water diffusivity was in some cases higher (around ±15%) due to the existence of an overlap between the NMR line of water and those of ions.

Results and Discussion

An example of ^{1}H NMR spectra of [Emim][ETSO4] containing water is shown in Fig.1. The spectra were recorded using the free induction decay NMR sequence. Due to high performance characteristics of our PFG NMR spectrometer the cation and anion lines at 1.5 ppm and 1.2 ppm, respectively, could be completely resolved. This allowed reliable measurements of the diffusivities of the cations and anions in a single PFG NMR experiment using these two lines. The recorded PFG NMR attenuation curves for the cation and anion lines at 1.5 ppm and 1.2 ppm were monoexponential in agreement with Eq.1. It was verified that for different "pure" lines of the cation (Fig.1) the measured diffusivities remained the same within the experimental uncertainty (±10% or better).

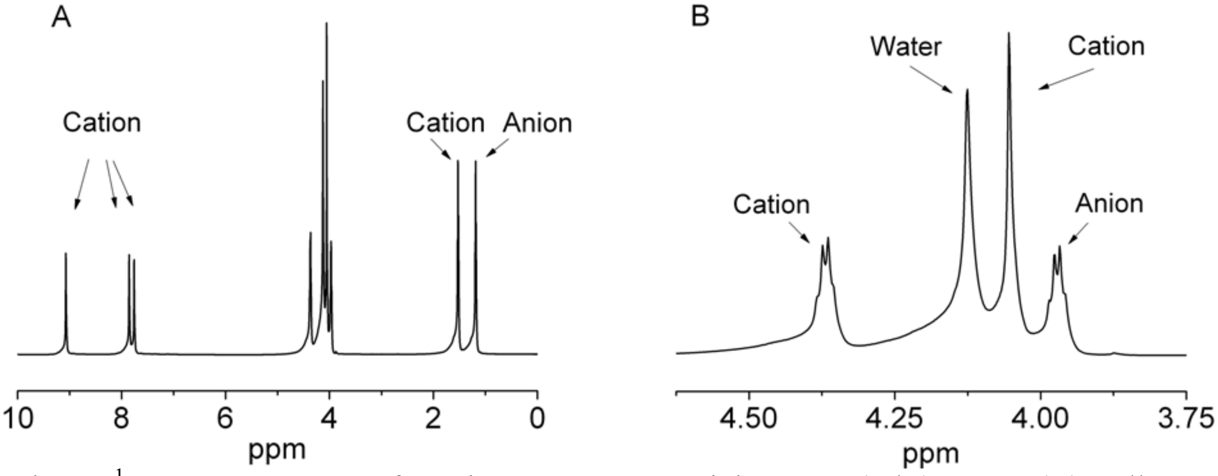

Fig. 1: ^{1}H NMR spectrum of [Emim][ETSO4] containing 10% (w/w) water: (A) Full ppm range showing all proton NMR lines, (B) Reduced ppm range to show lines between 4.75 and 3.75 ppm.

Fig.2 shows examples of the dependencies of the [Emim]$^+$ and [ETSO4]$^-$ diffusivities on water concentration in [Emim][ETSO4]. It is seen in Fig.2 that an increase in the water concentration from zero to approximately 0.7 water molecules per anion-cation pair strongly enhances the diffusion rates of the cations and anions. A further increase in the water concentration leads to a less pronounced increase in the ion diffusivities. The results in Fig.2 show that the diffusivity values of water in the [Emim][ETSO4] samples are much larger than those of the ions but, at the same time, much smaller than the corresponding diffusivity of pure water (2.3×10^{-9} m^2s^{-1} at 298 K) [26]. The water diffusivity was found to increase slowly with increasing water concentration (Fig.2). Comparison of the data in Fig.2 (a) and (b) indicate that the diffusivities of the ions and water increase with increasing temperature. This is an expected behavior that was previously observed for different types of RTILs including [Emim][ETSO4] [3-10, 19].

The results of recent studies indicate that the RTILs of the type examined in this work are expected to exhibit a well-defined nanostructural organization, *i.e.* polar regions, which are formed by the charged head groups of the cation and anion, and nonpolar regions, which are mostly formed by the tail groups of the cation [8, 13, 27, 28]. When a small amount of water is introduced into the water-free RTIL, water molecules are incorporated into the polar domains. These molecules are expected to form anion—HOH—anion type complexes through hydrogen bonding [8, 27, 29-31]. An observation of such hydrogen-bond formation for [Emim][ETSO4] was recently observed using computational and experimental approaches [10, 32, 33].

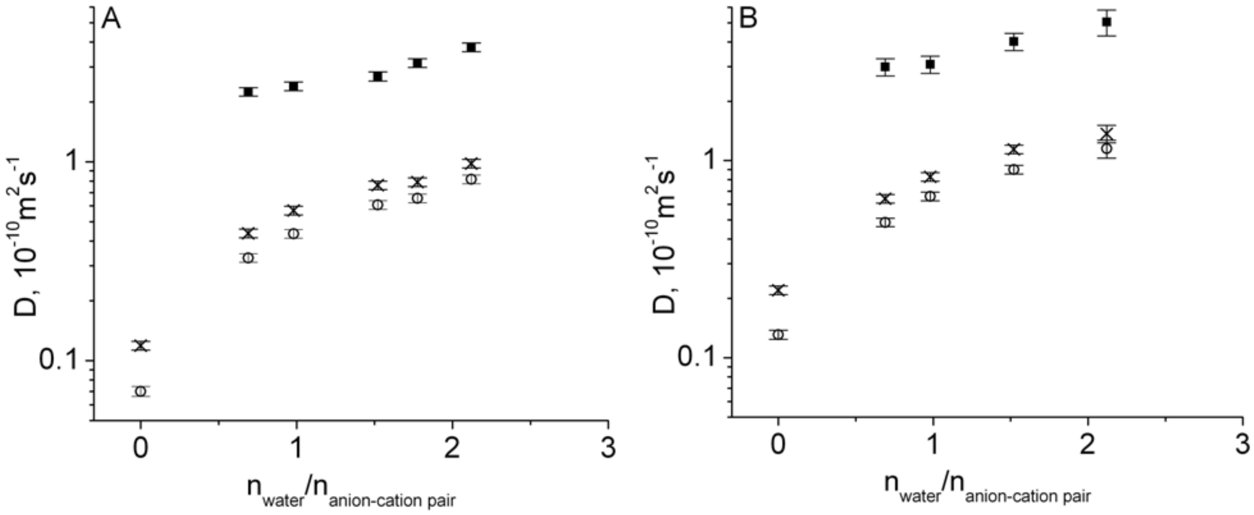

Fig. 2: Diffusivities of $[Emim]^+$ (×), $[ETSO4]^-$ (o), and water (■) measured by proton PFG NMR in [Emim][ETSO4] as a function of the number of water molecules per anion-cation pair ($n_{water} / n_{anion\text{-}cation\ pair}$): (A) at 298 K, (B) at 308 K.

The formation of water-anion complexes where water molecules mostly interact with the ions rather than with other water molecules in [Emim][ETSO4] is supported by the experimental observation that the water diffusivities in the studied samples (Fig.2) are in all cases much smaller than the diffusivity of pure water. As a result of the hydrogen-bond formation the electrostatic interactions between the cation head groups and the anions become partially screened by water [8-10, 27, 29-31]. Screening of the electrostatic interactions could be the main reason for the observed increase in the ion diffusivities (Fig. 2). The smallest non-zero water concentration used in this study (around 0.7 water molecules per anion-cation pair) was sufficiently large to ensure that all anions in the samples can form hydrogen bonds with water because each water molecule is capable of forming such bonds with two anions. As a result, an increase in the water concentration beyond this initial level would not lead to any increase in the number of the anions that directly interact with water molecules. This consideration provides a possible explanation for a less significant increase in the ion diffusivities with increasing water concentration when water concentration becomes larger than 0.5 water molecules per anion-cation pair.

It is seen in Fig.2 that in the water-free sample of [Emim][ETSO4] the diffusivity of the more bulky cation is approximately a factor of two larger than that of the less bulky anion. Such anomalous behavior was previously reported for imidazolium-based ionic liquids [3-10]. At the same time, for other types of ionic liquids a normal relationship between the size and diffusivity of diffusing species can also be observed, *i.e.* a larger cation was shown to diffuse slower than a smaller anion [19]. The results in Fig.2 show that the anomalous difference between the ion diffusivities in [Emim][ETSO4] decreases significantly with increasing water concentration. Strong electrostatic interactions in the water-free [Emim][ETSO4] ionic liquid are most likely responsible for the observed anomalous relationship between the diffusivities of the cation and anion. These interactions can lead to the existence of a well-defined local structure formed by the charged groups of the ions. As a result of the existence of such local structure the cation diffusion could show anisotropy (*viz.* different diffusivity values along different directions) on the length scale comparable with the size of this structure [6]. As discussed above, water molecules added to ionic liquids show an ability to screen the electrostatic interactions between cations and anions. As a result of such screening the local cation-anion structures can be disrupted [27, 30, 31] leading to a loss of the anisotropy for cation diffusion. It can be speculated that such loss of the diffusion anisotropy due to disruption of the local order is the primary reason for the suppression of the anomalous relationship between the diffusivities of $[\mathrm{Emim}]^+$ and $[\mathrm{ETSO4}]^-$ in [Emim][ETSO4]. Most recently, water-induced reduction in the extent of the anomalous relationship between the diffusivities of cations and anions was observed in molecular dynamics simulations of diffusion in imidazolium based ionic liquids [9, 10].

In conclusion, in this letter we report a PFG NMR observation of a suppression of the anomalous relationship between the diffusivities of the cation and anion in the imidazolium-based ionic liquid due to addition of water into this ionic liquid. This observation is tentatively explained by the disruption of a well-defined local order in the mutual arrangements of the cations and anions by water molecules.

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