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Diffusion in ionic liquids: the interplay between molecular structure and dynamics

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Diffusion in a series of ionic liquids is investigated by a combination of Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR). It is demonstrated that the mean jump lengths increase with the molecular volumes determined from quantum-chemical calculations. This provides a direct means—*via* Einstein–Smoluchowski relation—to determine the diffusion coefficient by BDS over more than 8 decades unambiguously and in quantitative agreement with PFG NMR measurements. New possibilities in the study of charge transport and dynamic glass transition in ionic liquids are thus opened.

Ionic liquids are under investigation for use as reaction media, in batteries and supercapacitors, solar and fuel cells, electrochemical deposition of metals and semiconductors, protein extraction and crystallization, nanotechnology applications, physical chemistry, and many others.[1–3] However, the interplay between the molecular structure and diffusivity in these materials remains unclear despite the fact that diffusion is one of the key processes determining the performance and technological applications involving ILs. In the current study, experimental and theoretical approaches are combined to investigate the quantitative relationship between the structure and dynamics in a series of ionic liquids. For the first time, we demonstrate that the mean ion jump length—a key quantity determining the ion mobility—increases with molecular volume of the ionic liquids investigated.

Diffusion is a ubiquitous and fundamental process characterized by the haphazard motion of elementary constituents of matter, most notably of atoms and molecules, due to their thermal energy. It maintains the functionality of living cells, determines the rates of chemical reactions, facilitates electrical conduction, and forms the basis of numerous technological applications.[4–6] Fick's first law of diffusion provides a means of explaining the process in terms of mass transport down a concentration gradient. Within this framework, the diffusive flux, j, is given by $j = -D(c)\nabla c$ where c denotes the concentration, D is the diffusion coefficient of the diffusants, and ∇ is a vector del operator. The concentration profile due to diffusion at time t can be determined upon consideration of the principle of mass conservation. This yields Fick's second law of diffusion expressed as $\partial c/\partial t = \nabla(D(c)\nabla c)$. This approach, although widely used, does not provide a direct link to the molecular structure of the material under consideration.

Einstein and Smoluchowski proposed a microscopic description of diffusion. According to this view, the particles (diffusants) haphazardly hop, executing random walk quantifiable through the Einstein–Smoluchowski relation (written as $\langle r^2\rangle = 6Dt$, where $\langle r^2\rangle$ represents the mean-square distance traversed by the diffusants in time t). The random motion of individual particles gives rise to a diffusive flux on a macroscopic level that can be described by Fick's laws of diffusion. It can be easily shown that the mean-square distance travelled by the diffusant at time t is expressed as $\langle r^2\rangle = N\langle\lambda_h^2\rangle$, where N is the total number of jumps and λ_h denotes the mean jump length. Therefore, the Einstein–Smoluchowski relation for a single rate-determining jump by the diffusant can take the form $\langle\lambda_h^2\rangle = 6D\tau$, where τ is the mean jump time to cover the characteristic mean jump length, λ_h[6]. Due to the sub-nanometric length-scales involved, it has not been possible to measure λ_h to date. In this study, we experimentally determine the characteristic mean jump lengths in a series of ionic liquids (see Scheme 1) by combining Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient NMR (PFG NMR). We also show that the values obtained increase with molecular volumes from quantum-chemical calculations.

Due to its ability to probe molecular fluctuations and charge transport in broad frequency and temperature ranges, BDS turns out to be a versatile experimental tool for probing charge transport in ionic liquids.[7–10] BDS measures the complex dielectric function, $\varepsilon^*(=\varepsilon' - i\varepsilon'')$, as well as the complex conductivity function, $\sigma^*(=\sigma' + i\sigma'')$. At low applied electric fields (within the linear response regime), the two functions are given by $\sigma^*(\omega,T) = i\varepsilon_0\omega\varepsilon^*(\omega,T)$, implying that $\sigma' = \varepsilon_0\omega\varepsilon''$ and $\sigma'' = \varepsilon_0\omega\varepsilon'$ where ε_0 and ω denote the permittivity of vacuum and radial frequency, respectively. It should be emphasized that BDS probes Brownian fluctuations as long as the measurements are conducted within the linear response regime. This makes it possible to compare the resulting diffusion coefficients (discussed later in the current article) to those obtained by PFG NMR.

Ionic liquids based on the bis(trifluoromethylsulfonyl)imide anion were synthesized with purity greater than 99%. The water content was

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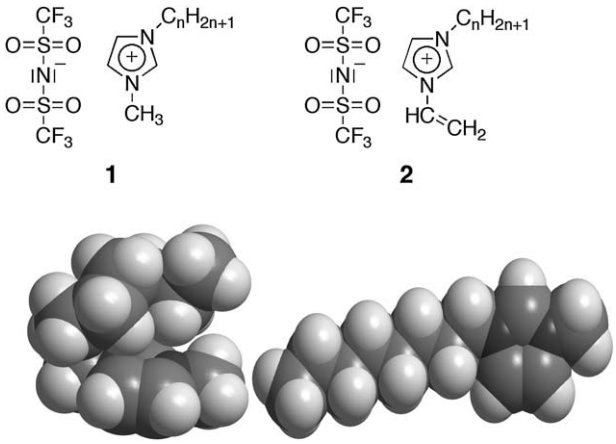

Scheme 1 Chemical structures of: (1) 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, *n*: 3 (PMIM), 4 (BMIM), 6 (HMIM), 8 (OMIM), and 10 (DMIM), and (2) 1-alkyl-3-vinylimidazolium bis-(trifluoromethylsulfonyl)imides, *n*: 5 (PVIM), and 8 (OVIM). Two possible conformations of the $[OMIM]^+$ cation are also shown.

determined by Karl Fischer titration and was found to be 400 ppm in $[BMIM][NTf_2]$, 1350 ppm in $[HMIM][NTf_2]$, 729 ppm in $[OMIM][NTf_2]$, 1240 in $[DMIM][NTf_2]$, 675 ppm in $[OVIM][NTf_2]$, and 830 ppm in $[PVIM][NTf_2]$. The imidazolium bis-(trifluoromethylsulfonyl)imides were obtained in quantitative yield from the corresponding imidazolium iodides (1 mole) in the case of the vinylimidazolium salts or the 1-propyl-3-methylimidazolium salt and lithium bis(trifluoromethylsulfonyl)imide (1.05 mole, from IOLITEC GmbH) by stirring water solution of the starting materials at room temperature for 16 h, phase separation, washing the resulting ionic liquid at least 3 times with water and drying *in vacuo* at 60 °C for 24 h in the case of the 1-alkyl-3-vinylimidazolium bis-(trifluoromethylsulfonyl)imides or at 80 °C for 24 h in the case of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides. A similar procedure was used for preparation of the 1-alkyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imides bearing a butyl group or a longer alkyl chain using the corresponding imidazolium chloride as starting material. The imidazolium iodides were made by stirring of either 1-vinylimidazole or 1-methylimidazole with the corresponding alkyl iodide in the presence of *tert*-butylmethylether under nitrogen at room temperature until full conversion of the imidazole derivative was obtained. The imidazolium chlorides were synthesized from 1-methylimidazole (1 mole) and the corresponding alkyl chloride (1 mole) by stirring the starting materials under nitrogen at 70 °C until full conversion of 1-methylimidazole. The resulting imidazolium halogenides were washed at least 3 times with equal volume of ethyl acetate and dried *in vacuo* at 40 °C in the case of the imidazolium iodides or at 60 °C in the case of the imidazolium chlorides for 16 h. The yield was 90–95% for the imidazolium halogenides.

A 400 MHz NMR spectrometer with a home-built gradient device has been used to obtain the self-diffusivities at different temperatures.[11] The stimulated spin echo pulse sequence with an observation time of 100 ms was used in accordance with suggestions of Annat *et al.*[12] The spin echo attenuation showed a mono-exponential behaviour, *i.e.* one-component diffusion over the whole temperature range examined.

Molecular volumes of the ionic liquids were obtained from optimized geometries using PM6 Hamiltonian as implemented in MOPAC2009.[13] To account for solvent effects the COSMO solvation model was applied[14] assuming a static dielectric permittivity of $\varepsilon = 15$ as a typical value for many imidazolium-based ILs.[15,16] Various conformations of the ions have been considered (*e.g.* 56 conformers for $[DMIM]^+$). Maximum molecular diameters, *d*, were obtained by taking the longest distance between two atoms and adding the van der Waals radii of the atoms. For the calculation of *V* as well as *d*, the van der Waals radii reported by Bondi[17] were assumed. The obtained molecular dimensions are summarized in Table 1. Given ranges correspond to the variation with conformation. The described technique is able to reproduce the well established ionic volumes of many common ions.[18] The values of this work appear to be systematically lower than volumes determined from crystal structures[19] but show the same trends. The latter values could only be reproduced by choosing different van der Waals radii.

Broadband dielectric measurements[20] were carried out using a Novocontrol high resolution alpha dielectric analyzer (0.1 Hz to 10 MHz) and an HP impedance analyzer (1 MHz to 1.8 GHz) in the temperature range 170 to 400 K, stabilized to better than 0.1 K by Quatro temperature controllers using pure nitrogen as heating agent.

The dielectric spectra of the ionic liquid $[OMIM][NTf_2]$ measured over a temperature range of more than 100 K are presented in Fig. 1. A pronounced frequency and a temperature dependence of the underlying mechanisms are observed. The real part of the complex conductivity σ' is characterized by a plateau at the intermediate frequency range (the value of which is the dc conductivity, σ_0) and the characteristic radial frequency, ω_c, at which the dispersion sets in and turns into a power law at higher frequencies. The systematic decrease of σ' from the σ_0 value at lower frequencies is due to the electrode polarization and is out of the scope of the current article. It is also worth noting that the real part of the complex dielectric function, ε', displays the usual features of a relaxation process at ω_c. The charge transport in ionic liquids is characterized by two main quantities obtained from the dielectric spectra, namely, σ_0 and ω_c. The spectra at different temperatures coincide upon scaling with respect to ω_c indicating that both electrode polarization (dominating the low frequency spectra) and bulk charge transport exhibit identical thermal activation.

Table 1 Molecular volumes, V_m, and maximum diameters, *d*, of the anion and series of cations determined from quantum-chemical calculations and mean jump distances, λ_h, for different conformations of the ions, constituting the ionic liquids. The ranges for molecular volumes and diameters correspond to the minimum and maximum values for the different conformations

Ion	V_m/nm^3	*d*/pm	λ_h[a]/nm
$[PMIM]^+$	0.1492–0.1524	989–1131	0.24
$[BMIM]^+$	0.1694–0.1738	1042–1260	0.26
$[PVIM]^+$	0.1982–0.2054	1084–1522	0.28
$[OVIM]^+$	0.2601–0.2722	1118–1905	0.33
$[OMIM]^+$	0.2483–0.2619	1030–1768	0.31
$[DMIM]^+$	0.2899–0.3139	1053–2021	Not determined
$[HMIM]^+$	0.2070–0.2370	1334–2433	0.29
$[(CF_3SO_2)_2N]^-$	0.1693–0.1748	1000–1027	Not determined

[a] Valid for the combination of the stated cation and the NTf_2 $[(CF_3SO_2)_2N]^-$ anion. The value for $[DMIM]^+$-based ionic liquid could not be determined because it crystallized.

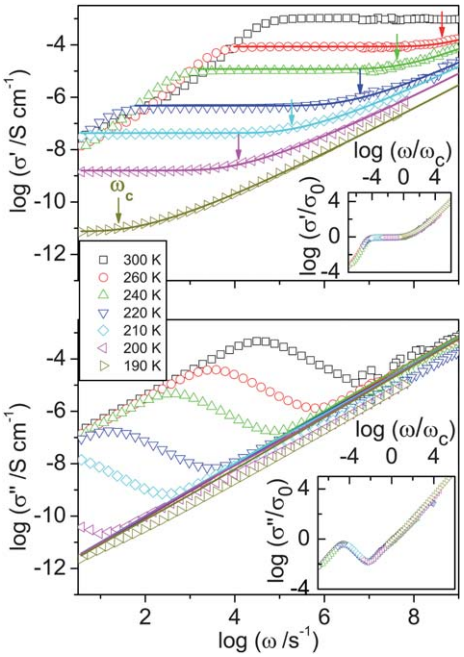

Fig. 1 Complex conductivity function $\sigma^*(=\sigma' + i\sigma'')$ of [OMIM][NTf$_2$] as functions of frequency at different temperatures. The corresponding characteristic radial frequencies, ω_c, are indicated by short vertical arrows on the spectra of σ'. The lines denote fits by the random barrier model.[21] The fit parameters obtained at different temperatures are as follows: (260 K: $\omega_e = 1.25 \times 10^8$ s^{-1}, $\sigma_0 = 8.6 \times 10^{-5}$ S cm^{-1}; 240 K: $\omega_e = 1.22 \times 10^7$ s^{-1}, $\sigma_0 = 1.2 \times 10^{-5}$ S cm^{-1}; 220 K: $\omega_e = 6.25 \times 10^5$ s^{-1}, $\sigma_0 = 4.8 \times 10^{-7}$ S cm^{-1}; 210 K: $\omega_e = 4.35 \times 10^4$ s^{-1}, $\sigma_0 = 4.3 \times 10^{-8}$ S cm^{-1}; 200 K: $\omega_e = 1.75 \times 10^3$ s^{-1}, $\sigma_0 = 1.6 \times 10^{-9}$ S cm^{-1}; 190 K: $\omega_e = 1.22 \times 10^1$ s^{-1}, $\sigma_0 = 7.6 \times 10^{-12}$ S cm^{-1}; and $\varepsilon_\infty = 6$). Inset: scaling with respect to ω_c and dc conductivity, σ_0, for the various temperatures. The error bars are comparable to the size of the symbols and the logarithm is to base 10.

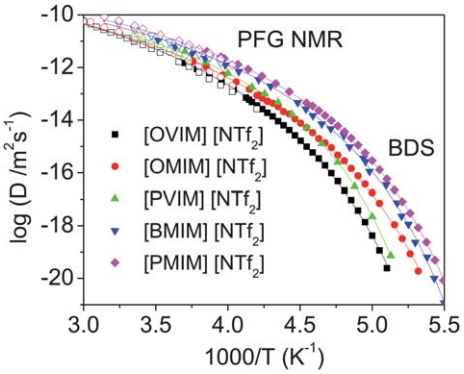

Fig. 2 Diffusion coefficients determined from broadband dielectric spectra by employing the Einstein–Smoluchowski equation (using ω_c as the characteristic hopping rate) and independently measured by PFG NMR (open symbols). The lines denote fits by the Vogel–Fulcher–Tammann equation.

By combining PFG NMR and BDS measurements, it is possible to calculate the characteristic mean jump length, λ_h, from diffusion coefficients (from PFG NMR) and rates ω_c (from BDS) at temperatures where the measurement windows of the two techniques coincide using the previously discussed Einstein–Smoluchowski relation. By that it becomes possible to access diffusion coefficients in a broad range spanning over 11 decades by employing BDS and PFG NMR (see Fig. 2). Consequently, electrical mobilities and effective number densities as well as their type of temperature dependence can be determined.[10] The diffusion coefficients presented in Fig. 2 are related to the mobilities, μ, through the Einstein's relation $\mu = qD/kT$, where q, k, and T refer to elementary charge, Boltzmann constant, and temperature assuming a mono-valent material. In what follows, we discuss the correlation between the diffusion rates, mean jump lengths and the molecular sizes, which is the main result of this article.

Diffusion is a rate process determined by the successful jumps over the rate-limiting energy barriers.[6] This may be quantified by $\omega_h = (kT/h)e^{-\Delta G/RT}$, where ω_h, h, ΔG, and R refer to the mean jump rate, Planck's constant, activation free energy, and gas constant, respectively. Based on similar premises, Dyre proposed a theoretical framework for quantitative description of charge transport in ion-conducting disordered materials.[21] According to this model, ion conduction proceeds through hopping of charge carriers (ions, in the case of ionic liquids) in a spatially randomly varying potential energy landscape. The attempt rate, ω_e, to overcome the highest energy barrier determining the dc conductivity, σ_0, is one of the characteristic parameters of the model. Since the dc conductivity is connected to the random motion of charge carriers the rates ω_h and ω_e are identical. The latter can be directly determined from broadband dielectric measurements. We have recently demonstrated that $\omega_e \cong \omega_c$ and Dyre's model quantitatively describe the dielectric spectra of ionic liquids up to the relaxation region.[7,8] For ionic liquids, ω_c has recently been shown to be equivalent to the structural relaxation rates determined by mechanical spectroscopy.[9] The characterization of the exact nature of the relaxation process is beyond the scope of the present study but recent investigations[22] suggest that this is a complex sequence of rotational and translational modes with the slowest process associated with cage fluctuations. Since the cage escape is prerequisite to steady-state translational diffusion the relation $\omega_e \cong \omega_h \cong \omega_c$ immediately follows.

A generally accepted quantitative description of the temperature dependence of the diffusion rate ω_c for glass-forming liquids does not exist.[20] Therefore, empirical approaches such as the Vogel–Fulcher–Tammann (VFT) equation are employed. Within this framework, ω_c can be expressed as $\omega_c = \omega_0 \exp(-D_V T_0/(T - T_0))$, where ω_0 is the value of ω_c in the high temperature limit,[6] T_0 denotes the ideal (Vogel) glass transition temperature, and D_V is a constant. The apparent activation energy ΔG in this case is clearly temperature-dependent. Based on the Einstein–Smoluchowski relation, it follows that the corresponding diffusion coefficients also exhibit a similar VFT-type thermal activation. This is exemplified in Fig. 2 for the bis-(trifluoromethylsulfonyl)imide-based ionic liquids investigated. It is also observed that the diffusion coefficients decrease with increasing the molecular volume, V_m, of the ionic liquid. The exceptional trend in [PVIM][NTf$_2$] at lower temperatures is traced back to partial crystallization and will not be considered further in the current discussion.

Fig. 3 shows the apparent activation energies ΔG for different ionic liquids based on the same bis(trifluoromethylsulfonyl)imide anion at different temperatures. ΔG increases remarkably with decreasing temperature. This implies that diffusion gradually slows down at lower temperatures. Higher molecular volumes result in increased ΔG. If other factors such as molecular packing remain the same, it is expected that translational diffusion of larger molecules requires more energy leading to enhanced ΔG values. However, to understand

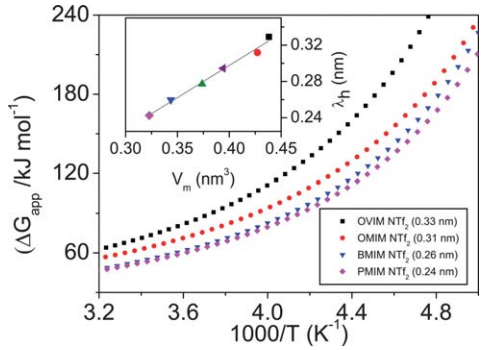

Fig. 3 The apparent activation energy, ΔG, of diffusivity in a series of bis(trifluoromethylsulfonyl)imide-based ionic liquids at different temperatures (determined from the VFT fits presented in Fig. 2). ΔG increases with the mean ion jump lengths (indicated in brackets). Inset: the mean jump lengths (from a combination of broadband dielectric spectroscopy and PFG NMR measurements) as a function of the molecular volume (from quantum-chemical calculations) of the ionic liquids investigated.

the link between the mean jump lengths and ΔG, we invoke the underlying predictions of the elastic models of glass-forming liquids.[23,24] Within these approaches, the heights of energy barriers controlling transport processes are determined by molecular rearrangement occurring on very short time scales. Recent experiments have confirmed the close link between fast and slow degrees of freedom in glass-forming liquids as predicted with the elastic models.[23,25,26]

According to the "shoving" model proposed by Dyre,[23] the activation energy $\Delta G(T) = V_c G_\infty(T)$, where V_c and G_∞ denote the temperature-independent characteristic volume and the instantaneous shear modulus respectively. This is consistent with the trend exhibited by the data presented in Fig. 3 illustrating the dependence of $\Delta G(T)$ on the molecular volume. In addition, the mean jump lengths are observed to increase with the molecular volumes (see the inset of Fig. 3) of the ionic liquids investigated. It should be noted that V_c is approximately the molar volume corresponding to the hopping process. Upon substitution of the obtained mean ion jump lengths (see Table 1 and Fig. 3; for instance, $\lambda_h = 0.25$ nm and $\Delta G = 200$ kJ mol^{-1}) as well as the activation energies shown in Fig. 3, one obtains a value of the instantaneous shear modulus of about 1 GPa. This is in the same order of magnitude as the experimental values obtained from Dynamic Mechanical Spectroscopy for numerous ionic liquids.[27]

Self-diffusion coefficients in a series of bis(trifluoromethylsulfonyl)imide-based glass-forming ionic liquids (ILs) are investigated in a wide frequency and temperature range by means of broadband dielectric spectroscopy (BDS), and pulsed field gradient nuclear magnetic resonance (PFG NMR). The mean ion jump lengths are experimentally determined for the first time and shown to increase with the molecular volumes determined from quantum-chemical calculations.

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