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Diffusion in Ionic Liquids: The Interplay Between Molecular Structure and Dynamics

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1. Introduction

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. However, the interplay between 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, Broadband Dielectric Spectroscopy (BDS), Pulsed Field Gradient NMR (PFG NMR), as well as molecular dynamics simulations are combined to investigate the quantitative relationship between structure and dynamics in a series of ionic liquids. For the first time, we demonstrate that the mean ion jump length – one of the key quantities determining the ion mobility - increases with molecular volume of the ionic liquids investigated [1].

Einstein and Smoluchowski proposed a microscopic description of diffusion. According to this view, the particles (diffusants) haphazardly hop, executing a 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. 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 by combining BDS and PFG NMR. We also show that the values obtained increase with molecular volumes from quantum-chemical calculations.

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 Figure 1). Consequently, electrical mobilities and effective number densities as well as their type of temperature dependence can be determined. The diffusion coefficients presented in Figure 1 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.

Diffusion is a rate process determined by the successful jumps over the rate-limiting energy barriers. This may be quantified by $\omega_c=(kT/h)e^{-\Delta G/RT}$, where ω_c, 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 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. We have recently demonstrated that $\omega_e \cong \omega_c$ and Dyre's model quantitatively describes the dielectric spectra of ionic liquids up to the relaxation region. For ionic liquids, ω_c has recently been shown to be equivalent to the structural relaxation rates determined from mechanical spectroscopy.

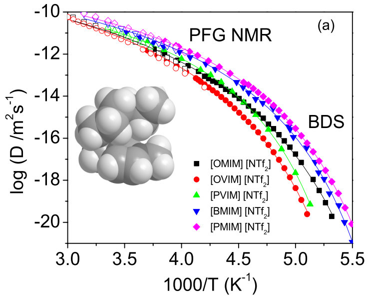

Fig. 1: Diffusion coefficients determined from broadband dielectric spectra by employing the Einstein-Smoluchowski equation (using ω_c as the characteristic hopping rate) and independently measured by PFG NMR (open symbols). The lines denote fits by the Vogel-Fulcher-Tammann equation. Inset: One of the possible conformations of the [OMIM] cation.

3. Conclusion

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 [1].

References

[1] J. R. Sangoro, C. Iacob, S. Naumov, J. Hunger, H. Rexhausen, R. Valiullin, V. Strehmel, R. Buchner, J. Kärger, F. Kremer, Soft Matter 7 (2011) 1678-1681.