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Broadband Dielectric Spectroscopy as a Tool to Study Diffusion Coefficients in Conducting Glass-Forming Systems

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1. Introduction

The transition from a fluid to a solid amorphous state which is observed as a liquid is super-cooled below its freezing temperature is gradual and presents one of the most significant open questions in condensed matter physics[1]. Quantitative understanding of molecular transport in the vicinity of calorimetric glass transition is therefore indispensable in this regard. Experimental studies of translational motion (diffusion coefficients, diffusion rates) as well as rotational (or structural) motion (viscosity, structural α-relaxation times) are necessary as they provide the most direct access to the molecular dynamics. However, no single experimental technique has been shown to simultaneously probe translational and rotational diffusion while giving information about the number density of diffusing components in this regime. In this work, a novel technique to determine diffusion coefficients in timescales ranging from pico-seconds to days by dielectric spectroscopy is presented. In addition, the mechanisms of charge transport and glassy dynamics are investigated.

2. Charge Transport and Glassy Dynamics in Ionic Liquids

Charge transport and glassy dynamics in the imidazolium based ionic liquids – are analyzed by combining Broadband Dielectric Spectroscopy (BDS), Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) and rheology. The dielectric spectra are dominated – on the low-frequency side – by electrode polarization effects while, for higher frequencies, charge transport in a disordered matrix is the underlying physical mechanism. Using the Einstein and Einstein-Smoluchowski equations enables one to determine – in excellent agreement with direct measurements by PFG NMR – the diffusion coefficient of the charge carriers. By that, it becomes possible to extract from the dielectric spectra **separately** the number density and the mobilities of the charge carriers and the type of their thermal activation (Fig. 1). It is shown that the observed Vogel-Fulcher-Tammann (VFT) dependence of the DC conductivity can be traced back to a similar temperature dependence of the mobility while for the number density an Arrhenius-type thermal activation is found. Extrapolating the latter to room temperature indicates that nearly all charge carriers are participating to the conduction process[2].

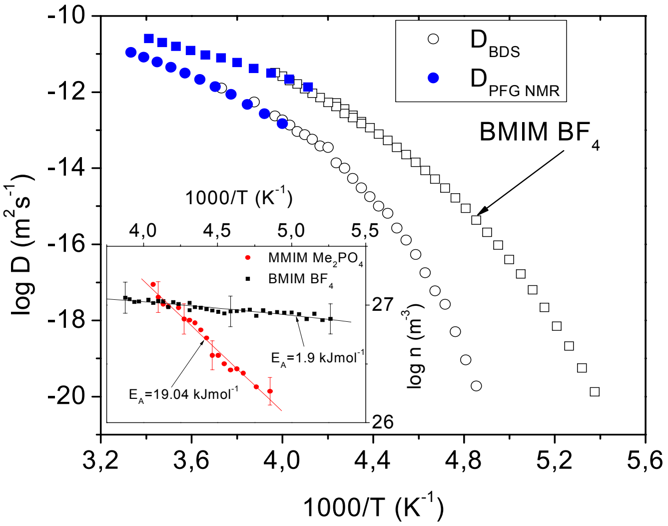

Fig. 1: Diffusion coefficient determined by the novel approach involving application of the Einstein-Smolukowski equation (using ω_c as hopping rate and with λ equal to the Pauling diameter of the ions as hopping length), compared with the diffusion coefficient measured by PFG NMR (in blue colour) for two ionic liquids: BMIM BF4 and MMIM Me2PO4 [2]. Inset: effective number of charge carriers as a function of inverse temperature (the respective activation energies are also indicated).

While the absolute values of dc conductivity and viscosity vary over more than 11 decades with temperature and upon systematic structural variation of the ILs, quantitative agreement is found between the characteristic frequency of charge transport and the structural α-relaxation. This is traced back to *dynamic glass transition assisted hopping* as the underlying mechanism of charge transport[3].

3. Conclusion

Diffusion coefficient in glass-forming ionic liquids (ILs) is investigated in a wide frequency and temperature range by means of broadband dielectric spectroscopy (BDS) and pulsed field gradient nuclear magnetic resonance (PFG NMR). It is experimentally shown that in the time-scale characterising the cross-over from sub-diffusive to diffusive ion dynamics, the hopping lengths are of the order of molecular diameters determined from quantum-chemical calculations. This provides a direct means – via Einstein-Smoluchowski relation – to determine diffusion coefficient by BDS over more than 8 decades unambiguously and in quantitative agreement with independent PFG NMR measurements. Unprecedented possibilities in the study of charge transport and dynamic glass transition are thus opened.

References

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