



# Translational dynamics of ionic liquid imidazolium cations at solid/liquid interface in gel polymer electrolyte

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## ABSTRACT

Gel polymer electrolyte (GPE) based on ethoxylated bisphenol A dimethacrylate and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF<sub>4</sub>]) ionic liquid (IL) at the mass ratio of 20:80 was prepared by *in situ* photopolymerization. The obtained material showed an exceptional behavior: its ionic conductivity was approximately twice higher than that of pure IL (as measured by impedance method). To explain the observed effect the translational diffusion of cations was studied indirectly by means of fast field-cycling (FFC) proton (<sup>1</sup>H) nuclear magnetic resonance (NMR) relaxometry method. The spin–lattice relaxation times of proton in cations were measured for neat IL and the IL involved in the polymer matrix in the temperature range from 248 to 343 K. The relaxation data obtained for bulk IL were analyzed in terms of both translational self-diffusion (*Torrey's model*) and local molecular reorientations around a long and a short molecular axis of the IL cation (*Woessner's model*). The relaxation of IL confined to polymer matrix revealed a low-frequency dispersion (not observed for bulk liquid) which is the fingerprint of the ionic liquid cations/polymer matrix interactions. Therefore, the low-frequency NMR relaxation data in GPE were analyzed assuming the *reorientation mediated by translational displacements* (RMTD) mechanism. This dynamic process allows to explain a very long correlation time of the order of 10<sup>-5</sup> s calculated for the cations at the polymer/IL interface and determine their diffusion coefficient. It was found that the latter is unexpectedly higher than that of the self-diffusion constant of cations in pure IL and/or inside pools of IL in the polymer matrix. This finding indicates that in the presence of the GPE matrix new cation-conducting pathways may be created which play an important role in ionic conduction at the microscopic and/or quasi-macroscopic scale.

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## 1. Introduction

Translational dynamics of particles (molecules or ions) has fundamental meaning for all important transport processes occurring in micro-scale in nature and therefore is extensively explored in different molecular systems [1–4]. For ionic liquids (ILs), the translational modes of the molecular dynamics of ions potentially provide the information on interionic interactions or molecular rearrangements reflecting complex diffusion processes associated, among others, directly with ionic conductivity [5–7]. For electrochemical use of ionic liquids, it is particularly important to find correlations between

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the motions and interactions of IL ions occurring at the molecular level and relate them to the macroscopic scale giving substantial arguments for further development, for instance, of alternative IL-based electrolytes used in electrochemical devices, such as solid-state batteries, capacitors, fuel cells, energy storage, and chemical sensors [8–15].

*In situ* photopolymerization is especially attractive method of preparation of novel solid polymer electrolytes with ionic conductivity suitable for practical applications (above 1 mS/cm) [16–20]. This technique involves photocuring of a homogeneous mixture composed of a monomer (the polymer matrix precursor) and an IL, and enables preparation of a gel polymer electrolyte (GPE) in a few minutes. It is also important to emphasize that the *in situ* method provides precise control of composition of the resulting GPEs [21,22], as opposed to the soaking method, where the amount of liquid electrolyte absorbed by a polymer matrix is difficult to control [23].

Morphology of the IL-containing GPEs can differ, depending on the compatibility of the polymer matrix and the IL used. GPEs can show phase separation, partial phase separation or can be homogeneous. According to our results [24] phase separation plays a crucial role in obtaining of high GPE conductivity since it is necessary to render pathways continuous for ion transport.

In this paper we applied the photopolymerization technique to obtain highly conductive GPE with separated polymer and IL phases. The matrix precursor was bisphenol A ethoxylate (2 EO/phenol) dimethacrylate (bisAEA4) and the IL was 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF<sub>4</sub>]). The obtained heterogeneous material showed exceptional behavior: its ionic conductivity at 25 °C (6.5 mS/cm) was almost twice higher than that of pure IL (3.76 mS/cm). Similar results were obtained by us also for other polymer electrolytes [21,22]. The aim of the present work was to explain the observed enhancement of the ionic conductivity in the context of the ionic diffusion at the *polymer/IL interface* formed on the border of the solid polymer phase and ionic liquid one.

From the ionic conductivity point of view, the transport of both cations and anions across the polymer electrolyte should be considered. Despite the fact that in ideal ILs all ions are fully dissociated, in real liquids they are to some extent aggregated and do not contribute to the overall electric conductivity [25]. Moreover, the differentiation of both cation and anion contributions to the overall ionic conductivity is extremely complicated exclusively on the basis of the quasi-macroscopic measurements applying an electrical stimulus. In this aspect, nuclear magnetic resonance (NMR) method is more sensitive and especially more selective one which allows to determine separately the microscopic ion dynamics. The advantage of this method over other ones is that it can be employed in a number of ways, including spectroscopy, diffusometry or relaxometry, to provide a variety of information, but first of all, it allows selective identification of the dynamic properties of each type of ions if only the anions and cations are differentiated by their own “NMR-active” nuclei [7,26–28]. Using commercially available NMR spectrometers the diffusion measurements are carried out routinely, particularly in liquids and soft matter, by applying the pulsed magnetic field gradient (up to 30–40 T/m) that encodes the spatial information about nuclear spins travelling with molecules [29]. Another gradient NMR method applying static magnetic field gradient (even up to 180 T/m) has considerably expanded the perspectives for the measurements of small self-diffusion coefficients (down to about 10<sup>-15</sup> m<sup>2</sup>/s) in supercooled liquids or molecular crystals, long chain polymer dynamics, restricted diffusion in systems of confined mesoscopic geometries or anomalous diffusion on fractal structures [30]. The pulsed and static field gradient NMR techniques can be classified as direct ones because the diffusion coefficients are determined directly from the NMR signal attenuation, recorded as a function of the magnetic field gradient strength and/or the time at which the diffusion is followed. Recently, the fast field-cycling (FFC) NMR relaxometry technique has been also successfully used for characterization of the translational diffusion, especially in liquid and soft systems [4,26,27,31,32]. This indirect and non-gradient method gives the possibility to determine the diffusion coefficient from measured frequency dependency (dispersion profile) of spin–lattice relaxation time by applying a suitable theoretical model describing the dynamics of the molecules (ions). Contrary to the gradient techniques, the relaxometry method is uniquely sensitive to the NMR signal of the spin nuclei belonging to a low-abundant fraction of molecules as far as their molecular dynamics is significantly differentiated from that of the high abundant one. This is particularly evidenced for liquid molecules adsorbed at pore walls in porous materials where the NMR diffusometry applying pulsed-field gradient (PFG) plays a minor role, whereas the FFC NMR relaxometry allows to follow the diffusion of adsorbed molecules based on specific relaxation mechanisms [33].

In the present study we are particularly interested in the important issue of the molecular diffusion of IL ions in a gel polymer electrolyte. Especially, the ionic diffusion at the polymer/IL interface forming on the border of the solid polymer and ionic liquid phases is carefully examined. The translational diffusion of the ions is studied by means of FFC NMR relaxometry. It should be emphasized that applying the nuclear magnetic resonance relaxometry method and proper theoretical models for the relaxation data we were able to distinguish the translational dynamics of the IL cations within the separated IL phase of GPE and of the cations interacting with the polymer matrix at the polymer/IL interface. It would be expected that the ion diffusion in the polymeric electrolyte should be slowed down as a result of confinement effects of the polymer matrix related to the geometrical restrictions of pores and/or IL-polymer matrix interactions. However, the obtained results have shown that the diffusion coefficient of the confined IL is comparable with that of neat IL. This result indicates that the cavities in the polymer matrix are large enough and do not restrict the translational diffusion of the IL molecules. On the other hand, the diffusion of the IL cations along the polymer matrix “surface” is significantly enhanced and the calculated diffusion constant is higher than that of pure IL.

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