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

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Introduction

Room temperature ionic liquids (RTILs) are salts which usually consist of bulky organic cations and inorganic anions. They are liquid at ambient temperature, have a negligible vapor pressure, and represent environmentally safe and non-corrosive media. These and other unique properties have raised increasing interest in applications of RTILs as a 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.

Experimental

^{1}H PFG NMR diffusion studies were performed with the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ([Emim][ETSO4]) using a wide-bore Bruker BioSpin spectrometer operating at a proton resonance frequency of 750 MHz. Diffusion data were obtained from dependencies of the intensity of the PFG NMR signal on the amplitude of the magnetic field gradients. 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.

Results and Discussion

Fig.1 shows examples of the dependencies of the diffusivities of cation ([Emim]+) and anion ([ETSO4]-) diffusivities on water concentration in [Emim][ETSO4]. The results in Fig.1 indicate that the anomalous difference between the ion diffusivities (*i.e.* the larger cation diffuses faster than the smaller anion) 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. 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. It can be speculated that such disruption of the local order is the primary reason for the observed suppression of the anomalous relationship between the diffusivities of $[Emim]^{+}$ and $[ETSO4]^{-}$ in [Emim][ETSO4].

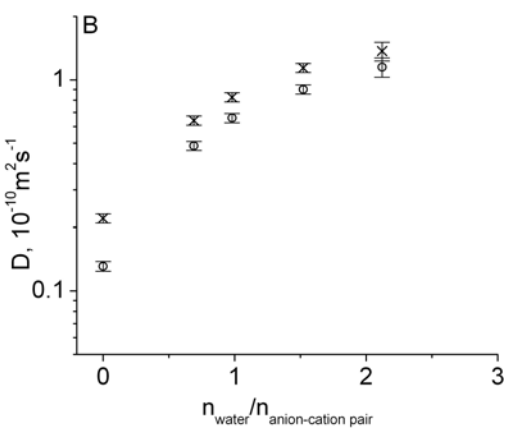

Figure 1: Diffusivities of $[Emim]^{+}$ (×) and $[ETSO4]^{-}$ (o) measured by proton PFG NMR in [Emim][ETSO4] as a function of the number of water molecules per anion-cation pair at 308 K.

Conclusions

Here 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.

Submitted Papers

[1] Menjoge, A.; Vasenkov, S., Langmuir 2008, submitted.