



Dynamic properties of water molecules in ionic liquid/water mixture with various alkyl chain length

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ABSTRACT

This work investigated the alkyl chain length dependence of dynamic properties of water molecules in imidazolium-based ionic liquid (IL)/water mixtures. The microscopic (i.e., self-diffusion coefficients of water molecule and ILs) properties of these systems suggested that the movement of IL/water mixtures decreases with increasing alkyl chain length of the IL. In contrast, the self-diffusion coefficient ratios ($D_{\text{water}}/D_{\text{anion}}$ or $D_{\text{water}}/D_{\text{cation}}$) at a water concentration extrapolated to 0 mol% (i.e., the value of a pure IL) increased as the alkyl chain length of the IL increased. This finding indicates that the water molecules in the IL/water mixtures move more independent of the IL as the alkyl chain length of the IL increases. Based on these results, we propose a plausible model for water molecules in a space within the IL.

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1. Introduction

Room temperature ionic liquids (ILs) have very unique characteristics, such as low-volatility, non-combustibility, high thermal stability and ionic conductivity [1]. One special feature of these compounds is the ease with which cations or anions can be interchanged, allowing ILs to be designed for specific purposes and enabling the fine-tuning of many physical properties (for example, as designer solvents). Of particular interest is the structural nano-heterogeneity of ILs. [2–4] The structure of imidazolium-based ILs is mainly composed of the nonpolar domain formed by alkyl chains and the polar domain formed by anions and imidazolium rings [3,4]. It is reported that as the alkyl chain length increases, the alkyl chains tend to aggregate and the nonpolar domain becomes thicker [3,4].

Many ILs are miscible with water over the complete concentration range from pure IL to pure water, and it is of interest to investigate mixtures of ILs and water because the macroscopic physicochemical properties of ILs are affected by the presence of water [5–7]. There have been many experimental and theoretical investigations of binary mixtures of water and ILs. Some of these studies provided experimental and theoretical evidence for the existence of water domains in the ILs [8–18]. In one recent report, Sieffert et al. [19] suggested the presence

of a local water pool where water molecules diffuse and rotate in the nano-heterogeneous structure of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₄MIM][TFSI])/water mixture based on MD simulation. Studying the same IL, Rollet et al. [20] obtained data for the self-diffusion coefficient at 0.3–30 mol% water by using pulsed field gradient spin-echo NMR, and suggested that the water pools are connected at the local scale. Subsequently, using small-angle neutron scattering (SANS) measurements, Gao et al. [21] investigated the microstructure of mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄MIM][BF₄]) and water at 70–84 mol% water and observed water nanocluster formation in the mixtures. Remarkably, Kashin et al. [22] succeeded in obtaining the morphology and formation dynamics of water-containing compartments in [C₄MIM][BF₄] at ~20 wt % directly by field-emission scanning electron microscopy. A variety of morphologies were detected and depended on the water concentration. In this manner, the presence of water domains in several ILs has been reported from various viewpoints. The nano-heterogeneous structure can be varied to some extent by changing the number of carbons in the alkyl chain of the IL.

However, how the water molecules behave in ILs with different alkyl chain lengths at very low water concentration, or extrapolated to 0 mol %, remains unclear. Motivated by these earlier reports and outstanding questions, herein we demonstrate the alkyl chain length dependence of the dynamic properties (self-diffusion) of water molecules in imidazolium-based ILs (1-alkyl-3-methylimidazolium tetrafluoroborate

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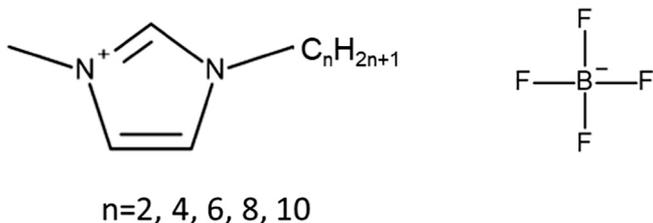


Fig. 1. Structures of 1-alkyl-3-methylimidazolium and the tetrafluoroborate.

([C_nMIM][BF₄], $n = 2, 4, 6, 8, 10$)/water mixtures by NMR measurements at room temperature.

2. Material and methods

Five alkyl chain length different ILs were purchased from the Kanto Chemical Co., Inc. and used as-received without further purification: 1-ethyl-3-methylimidazolium tetrafluoroborate ([C₂MIM][BF₄]), 1-butyl-3-methylimidazolium tetrafluoroborate, ([C₄MIM][BF₄]), 1-hexyl-3-methylimidazolium tetrafluoroborate, ([C₆MIM][BF₄]), 1-methyl-3-octylimidazolium tetrafluoroborate, ([C₈MIM][BF₄]), and 1-decyl-3-methylimidazolium tetrafluoroborate, ([C₁₀MIM][BF₄]), these purity are >95%, >95%, >99%, >99%, >98%. The ultrapure water used in experimental work was supplied by a Synergy UV system (Millipore Inc.). The molar percentage, x , of the water in mixtures with ILs. [C₂MIM][BF₄] and [C₄MIM][BF₄] were varied over the range from 0 to 100 mol% but [C₆MIM][BF₄], [C₈MIM][BF₄] and [C₁₀MIM][BF₄] were varied over the range from 0 to 75 mol% since they have a concentration range in which phase separation occurs at 298 K.

NMR study was carried out using an AVANCE III HD instrument (Bruker, 600 MHz). The ¹H NMR spectroscopy parameters were as follows: 20.0266 ppm spectrum width, 16,384 sample points, 10 s pulse delay, 8 scans, 0.18 Hz digital resolution. The ¹⁹F NMR spectroscopy parameters were as follows: 2.9998 ppm spectral width, 8192 sample points, 10 s pulse delay, 8 scans, 0.21 Hz digital resolution. The pulse-

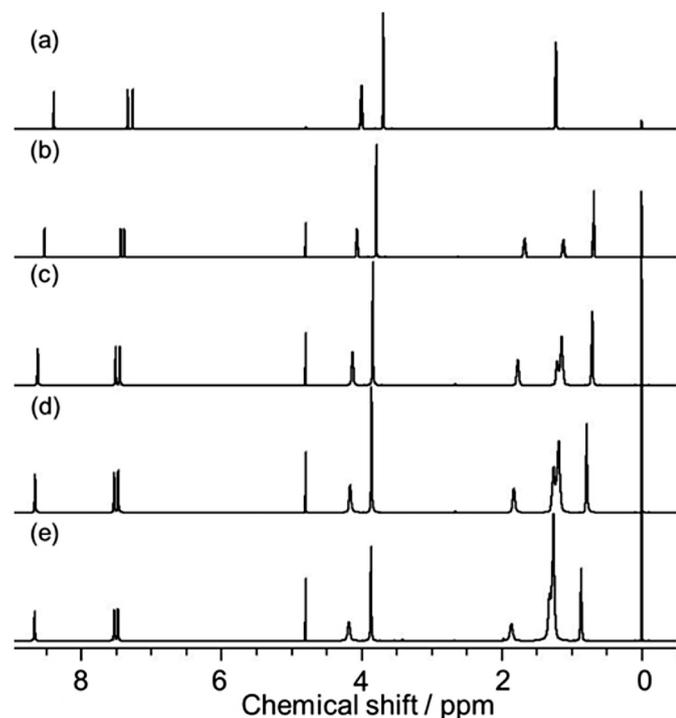


Fig. 2. ¹H NMR spectra of pure ILs at 298 K: (a) [C₂MIM][BF₄], (b) [C₄MIM][BF₄], (c) [C₆MIM][BF₄], (d) [C₈MIM][BF₄], (e) [C₁₀MIM][BF₄]. The peak around 4.8 ppm is H₂O in the internal standard solution.

gradient spin-echo (PGSE) NMR measurements were made using an AVANCE III HD instrument (Bruker, 600 MHz) at 298 K. The ¹H and ¹⁹F spectra were measured using a BBFO probe. The measurements of the self-diffusion coefficients for the cation and anion in each IL were made using ¹H and ¹⁹F nuclei, respectively. The stimulated echo sequence was used for the self-diffusion measurements.

The self-diffusion coefficient (D) was calculated by plotting the echo attenuation (E) according to Eq. (1) for a single diffusing species [23],

$$E = \exp\left(-\gamma^2 g^2 \delta^2 D (\Delta - \delta/3)\right) \quad (1)$$

where γ is gyromagnetic ratio, g is magnetic field gradient strength, δ is the duration of the gradient pulse, and Δ is the interval between the gradient pulses. In the present experiments, Δ was set to 15–2000 ms, the δ was set to 1.5 ms and g (16 different points) ranged from 3 mT/m to

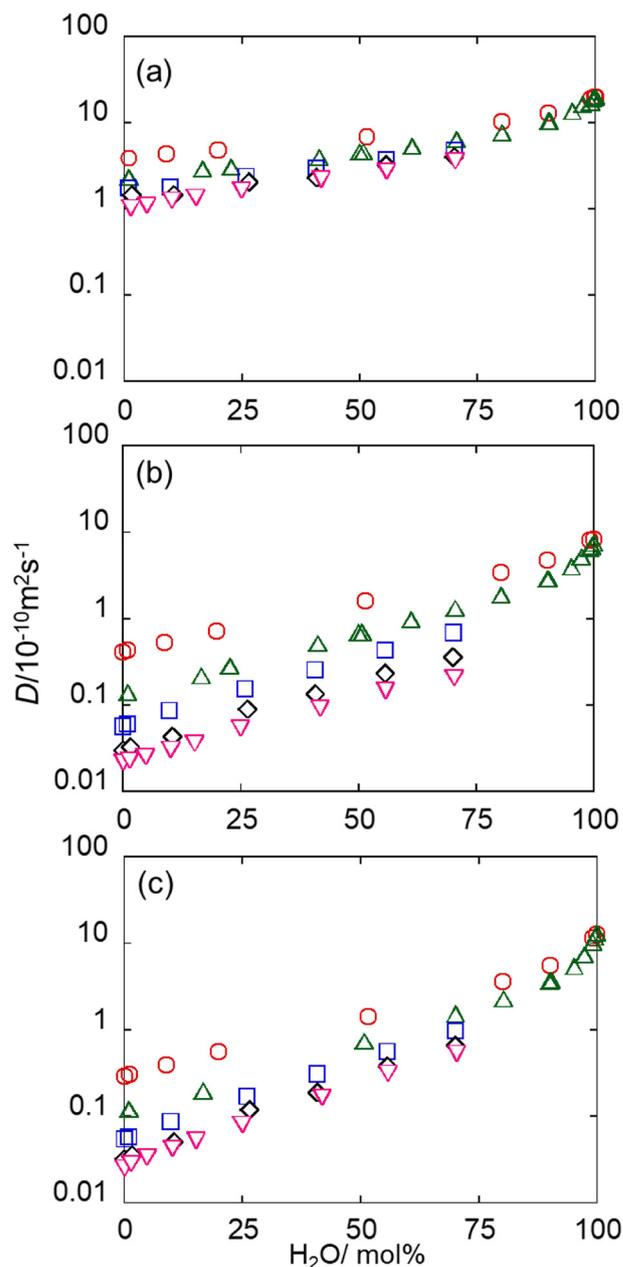


Fig. 3. Self-diffusion coefficients (D) of IL anions, cations and water at various concentrations of water at 298 K: (a) water, (b) cation, (c) anion. Legend: (○) [C₂MIM][BF₄]; (△), [C₄MIM][BF₄]; (□) [C₆MIM][BF₄]; (◇) [C₈MIM][BF₄]; (▽) [C₁₀MIM][BF₄].

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