

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/262051218>

Translational Diffusion in Mixtures of Imidazolium ILs with Polar Aprotic Molecular Solvents

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · MAY 2014

Impact Factor: 3.3 · DOI: 10.1021/jp501561s · Source: PubMed

CITATIONS

4

READS

58

5 AUTHORS, INCLUDING:



Bogdan Marekha

Université des Sciences et Technologies de Lill...

18 PUBLICATIONS 18 CITATIONS

SEE PROFILE



Oleg N. Kalugin

V. N. Karazin Kharkiv National University

74 PUBLICATIONS 398 CITATIONS

SEE PROFILE



Idrissi Abdenacer

Université des Sciences et Technologies de Lill...

107 PUBLICATIONS 559 CITATIONS

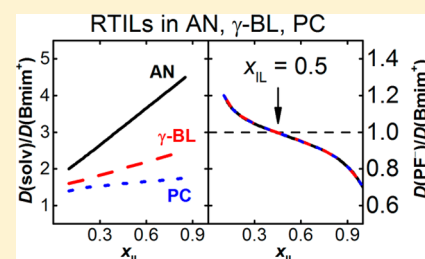
SEE PROFILE

Translational Diffusion in Mixtures of Imidazolium ILs with Polar Aprotic Molecular Solvents

Bogdan A. Marekha,^{†,‡} Oleg N. Kalugin,^{*,†} Marc Bria,[§] Richard Buchner,^{||} and Abdenacer Idrissi^{*,‡}[†]Department of Inorganic Chemistry, V.N. Karazin Kharkiv National University, Svoboda sq., 4, Kharkiv 61022, Ukraine[‡]University Nord de France, Lille1, LASIR (UMR CNRS A8516), Bât. C5, 59655 Villeneuve d'Ascq Cedex, France[§]University Nord de France, Lille1, CCM RMN, Bât. C4, Villeneuve d'Ascq 59650, France^{||}Institute of Physical and Theoretical Chemistry, University of Regensburg, 93040 Regensburg, Germany

S Supporting Information

ABSTRACT: Self-diffusion coefficients of cations and solvent molecules were determined with ¹H NMR in mixtures of 1-*n*-butyl-3-methylimidazolium (Bmim⁺) tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), trifluoromethanesulfonate (TfO⁻), and bis(trifluoromethylsulfonyl)imide (TFSI⁻) with acetonitrile (AN), γ -butyrolactone (γ -BL), and propylene carbonate (PC) over the entire composition range at 300 K. The relative diffusivities of solvent molecules to cations as a function of concentration were found to depend on the solvent but not on the anion (i.e., IL). In all cases the values exhibit a plateau at low IL content ($x_{\text{IL}} < 0.2$) and then increase steeply (AN), moderately (γ -BL), or negligibly (PC) at higher IL concentrations. This behavior was related to the different solvation patterns in the employed solvents. In BmimPF₆-based systems, anionic diffusivities were followed via ³¹P nuclei and found to be higher than the corresponding cation values in IL-poor systems and lower in the IL-rich region. The inversion point of relative ionic diffusivities was found around equimolar composition and does not depend on the solvent. At this point, a distinct change in the ion-diffusion mechanism appears to take place.



1. INTRODUCTION

Room-temperature ionic liquids (RTILs), being a very popular topic of scientific research during the last 15 years,^{1,2} are still of interest from various points of view, specifically in the field of physical chemistry.³ It is the wide range of possible properties that can be achieved by altering the constituting ions, which makes them so versatile in terms of applications^{4–6} and thus a challenge for researchers. RTILs possess a well-established set of useful properties, such as negligible vapor pressure, nonflammability, wide liquidus range, electrochemical stability, and high dissolving power toward both organic and inorganic matter, etc. However, their effective usage is partly hindered by several disadvantages of which the very high viscosity is the primary one, while difficulties in purification and rather high cost should also be mentioned.

One of the many potential applications suffering from the high viscosity (η) of RTILs, which is 2–3 orders of magnitude larger than that of conventional molecular solvents, is electrochemistry. Indeed, it is the mobility of ions, defining the main working parameter for electrochemical devices, electrical conductivity (κ), that is heavily affected by viscosity. The high viscosity of RTILs arises from strong long-range interionic interactions (i.e., it is their intrinsic property which cannot be substantially modified by changing the nature of constituent ions while maintaining other properties of interest). Moreover, possibly feasible temperature variations (ca. by less than 50 K) would only lead to reduction in viscosity by several

times.⁷ However, this point can be overcome by combining RTILs with low-weight molecular solvents, which not only leads to a reduction of viscosity but also generally extends the variety of properties and, thus, opens new application areas and a wider range of operating conditions. Reduced consumption of RTILs should be also mentioned in this perspective, keeping in mind their high cost.

For several families of RTILs (e.g., imidazolium- and pyrrolidinium-based ionic liquids), it was established that they are fully miscible with midpolar aprotic molecular solvents common for electrochemistry [e.g., acetonitrile (AN), propylene carbonate (PC), γ -butyrolactone (γ -BL), and others]. Numerous conductivity studies on a series of such mixtures^{8–12} revealed a maximum of κ at about $x_{\text{IL}} = 0.2$, while viscosity measurements showed monotonous behavior close to exponential^{10,13,14} on the molar fraction scale. The conductivity features were therefore attributed to ionic association phenomena.

By varying solvating power and viscosity of the solvent, one can tune the desired number of charge carriers and their mobility (i.e., the conductivity of a mixture), as it was noticed for mixtures of pyrrolidinium ILs with dipolar aprotic solvents.⁹ AN, γ -BL, and PC significantly differ in terms of their

Received: February 13, 2014

Revised: May 1, 2014

macroscopic polarity (relative permittivities at 298.15 K equal 35.96,¹⁵ 41.7,¹⁶ and 64.96,¹⁷ respectively), donicity (Gutmann's donor numbers at 298.15 K equal 14.1,¹⁸ 18.0,¹⁹ and 15.1,¹⁸ respectively) and viscosity (298.15 K values are 0.339,²⁰ 1.76,²¹ and 2.5120 mPa s,¹⁷ respectively) and, hence, can greatly modify the physicochemical properties of ILs, as it was shown, for example, by Couadou et al.²² With dependence on the desired set of properties, an optimized composition can be found that can be further used in electric double-layer capacitors and other electrochemical devices.^{11,23–26}

In this view, rational design of such systems (i.e., proper selection of the components and their concentrations) requires information about the key factors that define the composition dependence of the major transport properties of mixtures of RTILs with molecular solvents. Diffusion is a decisive factor not only for electrochemical applications but also for chemical reactions as well. Moreover, modern experimental methods allow observation of self-diffusion coefficients (D_i) for chemically nonequivalent species i . Such data can serve as a basis for developing a comprehensive picture of dynamics in such systems.

In contrast to conventional nonaqueous electrolyte solutions, where salt concentrations rarely exceed 0.2–0.3 in mole fraction units, imidazolium RTILs are fully miscible with most nonaqueous polar solvents. This gives an opportunity to follow the variation of many physicochemical properties, diffusivity in particular, over a much broader range of compositions: from very dilute solutions of RTILs through concentrated ones (which roughly corresponds to 'conventional electrolyte solution' regime) up to RTIL-rich mixtures where the molecular component is dispersed in the supra-molecular ionic network.

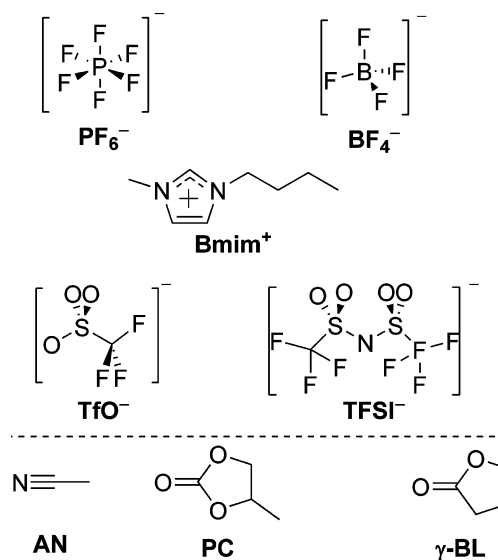
Since much attention in the field of RTIL-solvent mixtures has been paid to aqueous systems^{27–33} experimental diffusion-related studies on mixtures of RTILs with nonaqueous molecular solvents are rather scarce.

At present, there is still lack of microscopic information not only on the structure but also on the dynamics of ionic subsystem in mixtures of RTILs with nonaqueous (mid)polar aprotic solvents. This paper presents the results of a NMR-diffusometrical study on mixtures of 1-*n*-butyl-3-methylimidazolium (Bmim⁺)-based RTILs, namely 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate (triflate) BmimTfO, 1-*n*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide BmimTFSI, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate BmimPF₆, and 1-*n*-butyl-3-methylimidazolium tetrafluoroborate BmimBF₄, with AN, PC, and γ -BL (see Chart 1 for chemical structures) over the entire composition range. The rest of the paper is organized as follows: Experimental Section presents details of the sample preparation and the experimental procedure for diffusion measurements; general trends in experimental data are given a brief overview in Absolute Self-Diffusion Coefficients as a Function of Mixture Composition; the data is rationalized in terms of relative diffusion coefficients in Relative Self-Diffusion Coefficients Solvent-Cation as a Function of Mixture Composition; Relative Self-Diffusion Coefficients As a Function of Mixture Composition is devoted to the discussion of counterion diffusion in BmimPF₆-based mixtures; and finally, Conclusions are outlined.

2. EXPERIMENTAL SECTION

2.1. Materials. All the RTILs investigated in the present study were supplied by Solvionic (France) with a stated purity

Chart 1. Chemical Structures of the Ions Composing the Four Employed Ionic Liquids BmimBF₄, BmimPF₆, BmimTfO, BmimTFSI (Top), and the Molecular Solvents Used in This Study (Bottom)



of 99.5%. In accordance with the supplier, major impurities were not higher than 500 ppm for water, 10 ppm for halides, and 50 ppm for methylimidazole. It is well-known that overall purity and even traces of some particular impurities (namely, water and halides) can severely influence many properties of RTILs. Especially transport properties like viscosity³⁴ and, as shown by Umecky and colleagues, particle diffusivities,^{35,36} are very sensitive.

To minimize the effects of absorbed moisture, all RTILs were vacuum ($p < 10^{-6}$ bar) dried at 60 °C for at least 4 h prior to the preparation of solutions as this procedure is known to lower the water content below 200–500 ppm. Given the negligible halide content, no additional purification procedures were performed with the RTILs. PC (anhydrous, 99.7%, ≤ 20 ppm of H₂O) and γ -BL (ReagentPlus, 99.0%, ≤ 1000 ppm of H₂O) were supplied by Sigma-Aldrich, and AN (Rotisolv, 99.9%, UV-IR grade, ≤ 100 ppm of H₂O) was supplied by Carl Roth (Germany). γ -BL and AN were additionally dried with activated 4 Å molecular sieves, while PC was used without further purification.

All solutions were prepared in glass vials by weight in an Ar-filled glovebox, where the H₂O and O₂ content were kept below 2.5 ppm (v/v). To accelerate mixing, the solutions were sonicated for 30 min. Afterward solutions were transferred into 5 mm o.d. NMR tubes (supplied by Wilmad-LabGlass) fitted with a coaxial insert containing D₂O as NMR-lock solvent and parafilm. We employed a nonuniform concentration grid with more points taken around the composition corresponding to maximum conductivity in such mixtures (i.e., $x_{\text{IL}} \sim 0.15$).

2.2. NMR Measurements. All NMR measurements were performed on a Bruker Avance-II 400 spectrometer equipped with a 5 mm BBI probe with a z -gradient. Sample temperature was kept constant at 300.0 ± 0.1 K by means of VT-2000 Bruker variable temperature unit, which was calibrated with standard samples of 4% MeOH in MeOH-*d*₄ and 80% ethylene glycol in DMSO-*d*₆.³⁷ Prior to measurements, each sample was thermally equilibrated in the probe's acquisition zone for at least 15 min. Chemical shifts were referenced to the residual

Table 1. Experimental Self-Diffusion Coefficients (D) of the Neat Components Measured at 300 K and the Corresponding Literature Values Obtained by Different Methods^a

component	$D, 10^{-9} (\text{m}^2 \text{s}^{-1})$		
	this work	value	literature method
AN	5.1	4.85 (298.15 K) ^b	NMR
		4.31 (298.2 K) ^c	NMR, high-pressure diaphragm cell with trace [¹⁴ C]H ₃ CN
		4.37 (298.15 K) ^d	NMR
		4.34 (298.15 K) ^e	open-end-capillary
γ -BL	0.83	0.83 (303.15 K) ^f	NMR
		0.9 (303.15 K) ^g	NMR
		0.83 (295 K) ^h	NMR
PC	0.62	0.55 (303.15 K) ^f	NMR
		0.58 (303.15 K) ^g	NMR
		0.57 (298.15 K) ⁱ	NMR
		0.49 (298.15 K) ^j	NMR
Bmim ⁺ /TfO ⁻	0.018/–	0.52 (298.15 K) ^k	NMR
		0.019/0.014 (300 K) ^l	NMR
		0.0080/0.0059 (300 K) ^l	NMR
		0.0071/0.0054 (300 K) ^m	NMR
Bmim ⁺ /PF ₆ ⁻	0.0078/0.0066	0.016/0.015 (300 K) ^l	NMR
		0.0158/0.0146 (300 K) ^m	NMR
		0.01301/0.01292 (300 K) ⁿ	NMR
		0.016/– (298.15 K) ^b	NMR
Bmim ⁺ /BF ₄ ⁻	0.017/–	0.0299/0.0238 (300 K) ^l	NMR
		0.0282/0.0216 (300 K) ^m	NMR
Bmim ⁺ /TFSI ⁻	0.036/–		

^aExperimental temperatures are given in parentheses. ^bRef 44. ^cRef 45. ^dRef 46. ^eRef 47. ^fRef 48, estimated from a digitized graph. ^gRef 49. ^hRef 50. ⁱRef 51. ^jRef 52. ^kRef 53. ^lInterpolated using equations from ref 7. ^mRef 54. ⁿRef 55.

signal of the internal-lock solvent for ¹H and to the external 85% H₃PO₄ for ³¹P. Diffusion coefficients were measured with the standard Bruker ledbp2s pulse sequence originally developed by Wu et al.³⁸ Measurements with this pulse sequence were shown to be free of artifacts from thermal convection when used with sample rotation,^{39,40} as done in our experiments. The ledbp2s pulse sequence is of stimulated-echo type and, hence, also satisfies recommendations from Annat et al.⁴¹

Gradients were separately calibrated using known diffusion coefficient of residual HDO in D₂O.⁴² Typical NMR-diffusion experiments employed 16 acquisition scans with a gradient pulse length (δ) of 1.2–5 ms and a diffusion delay (Δ) of 100–200 ms. These parameters were adjusted to achieve ~95% attenuation of the signal at the highest gradient strength. The latter was varied in 16 steps up to ~50 G cm⁻¹ in a way that its squared value changed in equal increments. Gradient pulses were of squared sine shape, gradient recovery, and longitudinal eddy-current delays equaled to 0.2 and 5 ms, respectively. According to the literature, radio frequency pulse length and relaxation delay do not severely influence reliability of the results.⁴⁰ Nevertheless, rough estimations of these parameters were performed for each sample. As these characteristic times were found to depend significantly on concentration, they were optimized to ensure accurate results.

Selected samples were tested at different diffusion delays to ensure the absence of thermal convection effects.³⁹ The data was analyzed with the standard TopSpin T1/T2 relaxation utility by fitting the decay of the integral intensity of the corresponding signal to the Stejskal–Tanner equation⁴³ (eq 1)

$$A = A_0 \exp \left[-\gamma^2 \delta^2 g^2 D \left(\Delta - \frac{\delta}{3} \right) \right] \quad (1)$$

which relates the attenuated signal amplitude (A) with its nonperturbed value (A_0) using the gyromagnetic ratio of the probe nucleus (γ), gradient strength (g), gradient pulse length (δ), diffusion delay time (Δ), and self-diffusion coefficient of the diffusing particle (D).

The accuracy of our data can be judged by comparing our results for the pure components with literature values (Table 1). Generally, rather good agreement was achieved for the pure RTILs despite calibrating the gradient strength with a standard having a 2 orders-of-magnitude higher self-diffusion constant.

3. RESULTS AND DISCUSSION

3.1. Absolute Self-Diffusion Coefficients as a Function of Mixture Composition. The composition dependence of diffusion coefficients for liquid mixtures, including electrolyte solutions, can be interpreted with various approaches.⁵⁶ Currently, no strict theoretical framework is available that would predict and explain diffusivities of the constituents in ion-molecular systems over a broad range of concentration. As a result, most studies concerning diffusion in conventional electrolyte solutions and mixtures of RTILs with molecular solvents almost exclusively operate with general considerations and/or employ very simplistic models that hardly represent all the complexity and peculiarities of such systems.

For all 12 mixtures studied, the self-diffusion coefficients of all species (cations, anions, and solvent molecules) roughly follow a linear behavior in a semilogarithmic representation at the molar fraction scale (see sample data sets for BmimPF₆–AN, BmimPF₆–PC, and BmimBF₄–AN systems in Figure 1, all

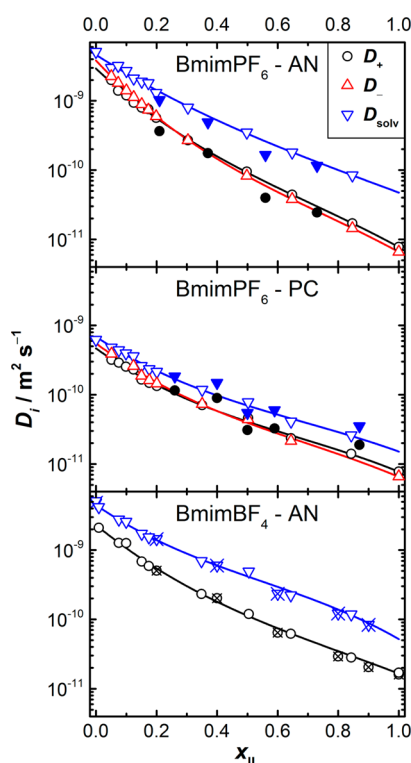


Figure 1. Experimental self-diffusion coefficients of the solvent molecules D_{solv} , cations D_+ , and anions D_- as a function of RTIL molar fraction in mixtures BmimPF₆–AN (top), BmimPF₆–PC (middle), and BmimBF₄–AN (bottom). Lines represent cubic fits of experimental data to eq 2. Solid symbols show data from Hsu et al.,⁵⁸ while the crossed ones are from Liang et al.⁴⁴ for comparison. Note logarithmic scaling in diffusion dimension.

data are collected in Table S1 of the Supporting Information) (i.e., diffusivities exponentially decrease with increasing RTIL mole fraction). Over the entire composition range, solvent molecules move several times faster than the ionic species. On the other hand, cations and anions exhibit comparable mobilities. The latter observation is usually considered as a manifestation of strong correlation in ionic motion due to high density of charged species.^{30,57} It should also be pointed out that the diffusion coefficients of all particles vary over 1.5–2 orders of magnitude with concentration.

For comparison, data of Hsu et al.⁵⁸ and the very recent results from Liang et al.⁴⁴ are included in Figure 1. Absolute values of our diffusion coefficients for cations and solvent molecules compare very well with the literature, and this agreement becomes excellent when relative diffusion coefficients are considered (see Figure 2 and discussion in Section 3.2).

For an empirical description of the concentration dependence, experimental logarithmic diffusion coefficients were fitted to a third-order polynomial in accordance with eq 2:

$$\log D = \sum_{i=0}^3 a_i x_{\text{IL}}^i \quad (2)$$

Fitted parameters along with raw experimental data are collected in Table S2 of the Supporting Information.

At first glance, the observed trend, decreasing self-diffusion coefficients with increasing RTIL concentration, is a consequence of the exponential viscosity increase upon RTIL

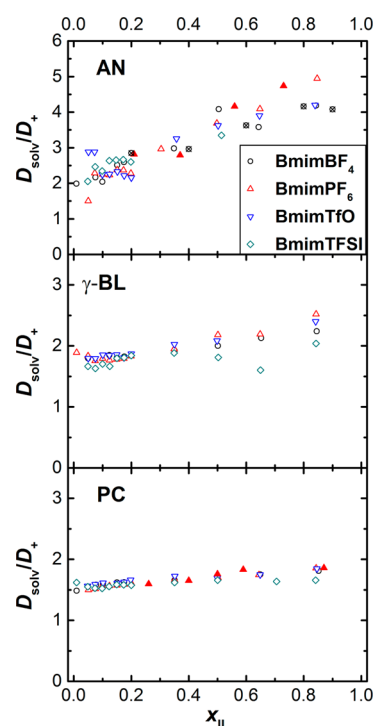


Figure 2. Ratio of self-diffusion coefficients for solvent molecules and cations as a function of RTIL molar fraction (open symbols). Solid symbols show results of Hsu et al.,⁵⁸ while the crossed ones are from Liang et al.⁴⁴ for comparison.

addition.^{14,34} Scharf and co-workers⁵⁷ studied HexmimTFSI in the low-polarity and thus strongly ion-pairing solvent CDCl₃ and in moderately polar DMSO-*d*₆ at rather high dilutions ($x_{\text{IL}} < 0.1$) by following the self-diffusion coefficients of the constituting ions, D_+ and D_- , over a broad temperature range (288–318 K). In DMSO-*d*₆, the ions were found to diffuse independently, with the respective diffusion coefficients being practically insensitive to changes in temperature and/or concentration. In contrast, motions of cations and anions in CDCl₃ revealed to be highly correlated. The values of D_+ and D_- were very close and exhibited a simultaneous rapid increase at very high dilutions opposite to the monotonous decrease of viscosity. These observations not only imply strong ion-pairing but significant ionic aggregation toward even bigger clusters.

3.2. Relative Self-Diffusion Coefficients Solvent-Cation as a Function of Mixture Composition. In their numerous studies on NMR-diffusometry of nonaqueous aprotic electrolyte (mainly Li⁺-based) solutions,^{48,49,59–62} Hayamizu and colleagues used the concept of proportionality between ionic and solvent diffusion coefficients as an indication for the validity of the Stokes–Einstein relation (i.e., that particle diffusion is only modulated by macroscopic viscosity changes). This idea is based on the generally observed proportionality between the diffusion coefficients of neat solvents and their fluidity ($= \eta^{-1}$). Viscosity, in turn, is considered to increase with concentration due to enhanced ion-molecular interactions. Any deviations from such proportionality were attributed to ionic association phenomena without detailed discussion. For the visual inspection of such details they proposed to plot the ratio of the diffusion coefficient of solvent molecules to that of ions as a function of concentration. It was anticipated that specific changes in ion-molecular and interionic interactions, if present, would cause an offset from a constant value. In accordance with

the Stokes–Einstein relation, the ratio should be defined by the inverse ratio of the hydrodynamic radii of the diffusing species.

This methodology of using the ratio of diffusion coefficients, introduced by Hayamizu et al.,^{48,49,59–62} has been used for several diffusion studies of aqueous mixtures of RTILs^{28,31} over a broad range of concentrations. In their study of BmimPF₆ mixed with various nonaqueous solvents, Hsu et al.⁵⁸ pushed this approach further by proposing the so-called “aggregation index”, defined as the diffusion ratio solvent–ion divided by the reciprocal of the corresponding radii ratio. The latter was estimated on the basis of quantum-mechanical calculations. They discovered that on dilution and/or heating, the aggregation index decreases but never reaches the limiting value of unity. The highest extent of screening of the interionic interactions (i.e., the smallest aggregation index) was observed for PC and DMSO, while AN was found to weaken ionic association only poorly. On the other hand, from the slope of the corresponding concentration trends an opposite conclusion can be reached: The steepest change in aggregation index was found for AN, whereas for PC it varied only slightly. This suggests that AN-based systems experience more pronounced changes when their composition is changed than those containing PC.

In order to avoid using poorly proven approaches, namely the highly questionable applicability of the Stokes–Einstein relation to RTIL-based systems,^{63–65} (vide infra) and the concept of hydrodynamic radius for such nonspherical particles as RTIL ions, which can also bear some degree of conformational flexibility, we will stick here to the diffusion ratios of Hayamizu and disregard the aggregation index of Hsu.

Figure 2 depicts the solvent-cation diffusion ratios as a function of mixture composition. Several clear observations should be pointed out. First, within experimental certainty, the ratio is practically independent of the anion for all three employed solvents. Despite the anticipated significant anion influence on the studied dynamical properties due to substantial diversity of anion sizes, shapes, symmetries, and charge distribution, it is not confirmed in the present study. This can be an indication of either negligible or less probable, non-negligible but indistinguishable influence of different anions on the solvation pattern of the cations, which is indirectly probed by the ratio of corresponding diffusion coefficients. This finding, however, does not rule out probable differences in ion-pairing tendencies of the studied RTILs that could be probed by other more accurate techniques. Second, in all three employed solvents, the ratio scatters around some solvent-specific constant value at low RTIL content ($x_{\text{IL}} < 0.2$) before rising with increasing RTIL concentration. Following Hayamizu, such concentration dependence is a sign of strong interionic interactions leading to ionic aggregation at higher concentrations. The low concentration plateau regime, in turn, corresponds to a state where the major factors determining particle diffusivities, namely their hydrodynamic size, mode of interaction with the microenvironment and microviscosity of the surrounding medium, either do not change or change simultaneously for cations and solvent molecules. This can be treated as a range of compositions, where dilute solution-like solvation pattern is maintained, which is modulated only by the general viscosity increase with increasing RTIL content. Third, the rise at high RTIL concentrations is most pronounced for AN (at $x_{\text{IL}} \approx 0.85$, solvent molecules diffuse 4–5 times faster than cations compared to $D_{\text{solv}}/D_{+} = 2.5$ at $x_{\text{IL}} < 0.2$), whereas it is less significant in γ -BL and almost negligible in PC. The

same order is observed for the magnitude of the low-concentration plateau value. This can be rationalized when comparing relative sizes of the solvent molecules and neat solvent properties. AN has the smallest molecule which results in higher value of the corresponding plateau value at $x_{\text{IL}} < 0.2$, as it is mainly determined by the relative sizes of the cation–solvent pair. γ -BL and PC have somewhat bigger molecules (see the Supporting Information) and, hence, lower D_{solv}/D_{+} plateau values. Also AN is the least polar and least donating solvent among the studied set, which suggests that its interaction with RTILs is more easily weakened with increasing RTIL concentration when compared to the cases of γ -BL and PC. This could be the reason for the steeper slope of the high concentration part of the relative diffusion coefficient dependence AN-cation as it implies more significant changes in the diffusion-determining factors with concentration. Thus, our observations are perfectly in line with those of Hsu et al. for BmimPF₆-based systems.⁵⁸ The fact that relative diffusion coefficients from different investigations agree better than the corresponding absolute values probably stems from probe calibration errors.⁶⁶

When considering diffusion models, the Stokes–Einstein (SE) relation (eq 3) is probably the most popular. It relates the self-diffusion coefficient (D) of a particle to its hydrodynamic radius (r) a factor (A) determining the hydrodynamic boundary conditions (stick, slip, or intermediate) and the medium viscosity (η).

$$D = \frac{kT}{A\eta r} \quad (3)$$

Accurate absolute values of the hydrodynamic radii of diffusing species can be estimated from data obtained by NMR experiments only if the gradient calibration of the probe was properly performed and the SE relation holds its relevance.⁶⁷ Originally, the SE relation was derived under the assumption of a large sphere moving in a structureless continuum whose molecules are negligible in size with respect to the diffusing particle. In mixtures of molecular solvents with RTILs, the representative diffusing species are of comparable sizes, so one has to expect that generally the SE relation would not be satisfied. Indeed, usually unrealistically low values of the hydrodynamic radii of individual ions are found no matter how the boundary condition is set.^{44,63–65}

In an attempt to check the applicability of eq 3 to the studied systems, we plot in Figure 3 for selected systems the effective Stokes radius $(Ar)_i = kT(D\eta\pi)^{-1}$ for cations and solvent molecules as a function of RTIL mole fraction. Viscosities were interpolated from experimental data by fitting logarithmic excess viscosities to a Riedlich-Kister type polynomial (see the Supporting Information for details). This representation, based on experimentally accessible quantities only, was chosen since there is no a priori knowledge of the hydrodynamic factor (A) for these systems. Moreover, it cannot be excluded that A varies with composition due to possible changes of diffusion mechanism, solution structure, and/or boundary condition. Figure 3 provides strong evidence that for the studied mixtures, viscosity grows faster than particle diffusivities decrease when the RTIL concentration is increased. According to theory, the A factor in eq 3 equals four for slip⁶⁸ and six⁶⁹ for stick hydrodynamic boundary conditions. Taking this into account, reasonable values of the hydrodynamic radii of cations and solvent molecules (3.65 Å for Bmim⁺ cation and 2.52, 2.95, and 3.06 Å for AN, γ -BL, and PC molecules, respectively), as

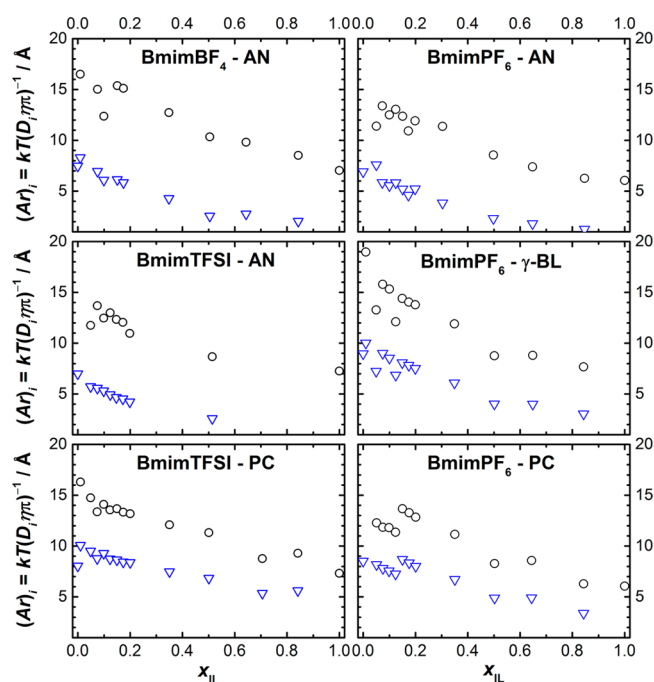


Figure 3. Estimated effective Stokes radii, A_r , for cations (black \circ) and solvent molecules (blue ∇) in selected mixtures as a function of the RTIL mole fraction.

estimated from quantum-chemical calculations of molecular volumes (see Supporting Information for details), can only be expected at very low RTIL content. Moreover, predicted effective radii of the ion pairs range from ca. 4.0 to 4.5 Å (see Table S4 of the Supporting Information), suggesting that it is rather individual cations than the ion pairs which are the representative diffusing entities containing cation at these mole fractions. At higher concentrations, the apparent hydrodynamic sizes progressively decrease down to unphysical values < 2 Å. We consider this as strong evidence for the inadequacy of the SE relation in concentrated mixtures of RTILs with molecular solvents and a clear indication of severe changes in solution microstructure and associated dynamics.

Such a monotonic decrease of effective radii with IL concentration was also observed in BmimBF₄/PF₆-PEG⁷⁰ and in RmimMeSO₃-H₂O mixtures.^{29,32} In the latter case, this was interpreted as an increase in the size of nonpolar domains formed by cation aggregates induced by the added solvent. In another recent study by Scharf et al.⁷¹ on EmimTFSI dissolved in organic solvents of different polarity at very high dilutions ($x_{\text{IL}} < 0.005$), the results of a Stokes–Einstein analysis of the observed ionic diffusivities were interpreted in terms of weighted averages of dissociated and ion-paired species. For the least polar employed solvent (CDCl₃), the authors even detected a second set of resonances that was attributed to large ionic aggregates with aggregation numbers reaching 10–20.⁷¹

3.3. Relative Self-Diffusion Coefficients as a Function of Mixture Composition. In the case of BmimPF₆-based systems, we were also able to follow anion diffusion by means of ³¹P nuclei. The so-obtained D_- values allowed us to calculate corresponding diffusivity ratios of solvent/anion and anion/cation, which are plotted together with already discussed solvent/cation ratios in Figure 4.

In contrast to the latter, solvent/anion ratios do not show a plateau at low concentrations (though more points are needed

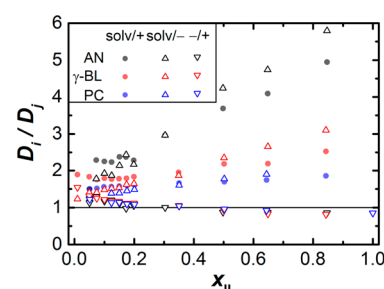


Figure 4. Ratio of diffusion coefficients for solvent molecules, cations, and anions in BmimPF₆-based mixtures vs the RTIL mole fraction.

to prove this) and rise more steeply. This results in an inversion of ionic diffusivities (i.e., at $x_{\text{IL}} < 0.5$ anions diffuse faster than cations), whereas in concentrated solutions and in neat ILs, the opposite is observed. Interestingly, the inversion trend is very similar for all the three solvents.

To the best of our knowledge, Hsu et al.^{58,72} were the first to pay attention to the observation that the unexpectedly low diffusivity of the smaller anions in pure RTILs can be enhanced more efficiently than that of the bigger cations by heating and/or dilution with molecular solvent. In other words, at a certain degree of dilution/heating an inversion is expected. On the basis of their various observations, mainly on BmimPF₆-based systems,⁵⁸ Hsu et al. proposed and later⁷² claimed the hypothesis of hyper-anion prevalence. The hypothesis implies that in pure RTILs and in concentrated solutions along with neutral ion aggregates, there are also (predominantly singly) charged associates. In accordance with this hypothesis, these charged aggregates are preferably enriched with anions. In other words, positively charged aggregates should be generally smaller in size than those with negative excess charge. Since NMR-diffusometry operates at a timescale of tens to hundreds of milliseconds, the observed self-diffusion coefficient is an apparent value averaged over all diffusing species. Thus, if one follows the hypothesis, anions are mainly localized in larger aggregates, which diffuse slower than the smaller cation-enriched aggregates. As a result, in pure RTILs and in concentrated solutions (where the native supramolecular network structure of the neat RTILs is maintained), $D_+ > D_-$, despite the opposite prediction from ion size. Upon dilution and/or heating, the aggregates get smaller and smaller until complete dissociation is reached and individual ions are the representative diffusing species. At this stage, the anticipated relative order of diffusion coefficients is found. This approach has also been used to explain similar observations on aqueous systems.²⁸

There are other explanations of the anomaly of ionic diffusion coefficients in pure RTILs in the literature. Stark et al., in their studies on RmimMeSO₃-H₂O mixtures,^{29,57} employed ideas of fast fluctuating nonpolar domains existing in neat RTILs and in concentrated solutions. The domains are considered to be composed of the alkyl moieties of the cations and to have a pseudomicellar structure. It was claimed that at the same hopping rate for counterions, cations have to pass longer distances between different aggregates than the anions which diffuse in between the aggregates. This should result in higher values for cation self-diffusion coefficients.

We believe that any speculation on details of ionic motions in such complex systems as RTILs and their mixtures with molecular components of different compositions should be based on some strong knowledge of diffusion mechanism. This

can be achieved by means of complementary use of rather sophisticated experimental (quasi-elastic scattering techniques) and simulation (well-parametrized molecular dynamics) methodologies which is still likely a “tabula rasa” in the field of RTILs. Urahata and Ribeiro⁷³ used equilibrium MD with a nonpolarizable force-field for singly charged RTILs of RmimHal and RmimPF₆ type to elucidate that cation diffusion is strongly anisotropic: compared to anion diffusion it is significantly enhanced in the direction perpendicular to the line connecting the imidazolium-ring nitrogen atoms in the ring plane. However, these results should be considered with caution as it has been frequently shown that significant polarization phenomena have to be taken into account to accurately capture dynamical properties of RTIL-based systems by means of MD simulations.^{74,75} Similar, but somewhat different results concerning the anisotropy of cation diffusion were obtained by Liu and Maginn⁷⁶ from MD simulations of BmimTFSI where ionic charges were downscaled by 20%. We stress the urgent need of such studies to shed light on the diffusion mechanism and on the nature of the diffusing particles. Our results prove that the inversion of diffusion coefficients is a kind of universal behavior in mixtures of RTILs with molecular solvents.

4. CONCLUSIONS

In the present study, mixtures of BmimBF₄, BmimPF₆, BmimTfO, and BmimTFSI with AN, γ -BL, and PC were studied over the entire composition range by means of NMR diffusometry at 300 K. Diffusion coefficients of the solvent molecules, cations, and anions progressively decrease with RTIL addition, roughly following the exponential viscosity increase. In a given solvent, the relative diffusion coefficients of solvent/cation (D_{solvent}/D_{+}) are independent of the anion. Data scatter around a constant value at $x_{\text{IL}} < 0.2$ and increase at higher concentrations. This increase is most pronounced for AN, less significant in γ -BL, and almost negligible in PC and may be an indication of rather strong cation solvation (both individual and/or in ionic aggregates) in γ -BL and PC over the entire composition range employed in this study.

From the observed variation of the effective hydrodynamic radius with composition, a significant change in solution structure and dynamics is expected for the mixtures of all three studied solvents. For the BmimPF₆-based system, a solvent-independent inversion of ionic diffusivities is observed around $x_{\text{IL}} \approx 0.5$. At low RTIL content anions diffuse faster than cations as anticipated from their relative sizes, whereas at high concentrations and in neat RTILs anion diffusion is slower. A separate study on the diffusion mechanism is needed to explain this rather universal behavior for RTIL-solvent mixtures.

■ ASSOCIATED CONTENT

Supporting Information

Tables of experimental diffusion coefficients for all studied systems, parameters of eq 2, details of viscosity, and molecular volume calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: onkalugin@gmail.com.

*E-mail: nacer.idrissi@univ-lille1.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by Ministry of Education and Science of Ukraine (Grant 0111U010518). B.A.M. is thankful to the French Government and Campus France agency for financial support. B.A.M., R.B., and A.I. also acknowledge support from the Centre de Coopération Universitaire Franco-Bavarois.

■ REFERENCES

- (1) Hallett, J. P.; Welton, T. Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508–3576.
- (2) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071–2084.
- (3) Endres, F.; Zein El Abedin, S. Air and Water Stable Ionic Liquids in Physical Chemistry. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101–2116.
- (4) Giernoth, R. Task-Specific Ionic Liquids. *Angew. Chem., Int. Ed.* **2010**, *49*, 2834–2839.
- (5) Torimoto, T.; Tsuda, T.; Okazaki, K. I.; Kuwabata, S. New Frontiers in Materials Science Opened by Ionic Liquids. *Adv. Mater.* **2010**, *22*, 1196–1221.
- (6) Patel, D. D.; Lee, J.-M. Applications of Ionic Liquids. *Chem. Rev.* **2012**, *12*, 329–355.
- (7) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 1. Variation of Anionic Species. *J. Phys. Chem. B* **2004**, *108*, 16593–16600.
- (8) Kalugin, O. N.; Voroshilova, I. V.; Riabchunova, A. V.; Lukinova, E. V.; Chaban, V. V. Conductometric Study of Binary Systems Based on Ionic Liquids and Acetonitrile in a Wide Concentration Range. *Electrochim. Acta* **2013**, *105*, 188–199.
- (9) Fox, E. T.; Paillard, E.; Borodin, O.; Henderson, W. A. Physicochemical Properties of Binary Ionic Liquid–Aprotic Solvent Electrolyte Mixtures. *J. Phys. Chem. C* **2013**, *117*, 78–84.
- (10) Canongia Lopes, J. N.; Costa Gomes, M. F.; Husson, P.; Pádua, A. I. A. H.; Rebelo, L. P. N.; Sarraute, S.; Tariq, M. Polarity, Viscosity, and Ionic Conductivity of Liquid Mixtures Containing [C₄im][Ntf₂] and a Molecular Component. *J. Phys. Chem. B* **2011**, *115*, 6088–6099.
- (11) Wang, H.; Liu, S.; Huang, K.; Yin, X.; Liu, Y.; Peng, S. BMIMBF₄ Ionic Liquid Mixtures Electrolyte for Li-Ion Batteries. *Int. J. Electrochem. Sci.* **2012**, *7*, 1688–1698.
- (12) Stoppa, A.; Hunger, J.; Buchner, R. Conductivities of Binary Mixtures of Ionic Liquids with Polar Solvents. *J. Chem. Eng. Data* **2009**, *54*, 472–479.
- (13) Li, W.; Zhang, Z.; Han, B.; Hu, S.; Xie, Y.; Yang, G. Effect of Water and Organic Solvents on the Ionic Dissociation of Ionic Liquids. *J. Phys. Chem. B* **2007**, *111*, 6452–6456.
- (14) Wang, J.; Tian, Y.; Zhao, Y.; Zhuo, K. A Volumetric and Viscosity Study for the Mixtures of 1-n-Butyl-3-Methylimidazolium Tetrafluoroborate Ionic Liquid with Acetonitrile, Dichloromethane, 2-Butanone and N, N-Dimethylformamide. *Green Chem.* **2003**, *5*, 618–622.
- (15) Barthel, J.; Bachhuber, K.; Buchner, R.; Gill, J. B.; Kleebauer, M. Dielectric Spectra of Some Common Solvents in the Microwave Region. Dipolar Aprotic Solvents and Amides. *Chem. Phys. Lett.* **1990**, *167*, 62–66.
- (16) Mialkowski, C.; Chagnes, A.; Carré, B.; Lemordant, D.; Willmann, P. Excess Thermodynamic Properties of Binary Liquid Mixtures Containing Dimethylcarbonate and γ -Butyrolactone. *J. Chem. Thermodyn.* **2002**, *34*, 1847–1856.
- (17) Barthel, J.; Neueder, R.; Roch, H. Density, Relative Permittivity, and Viscosity of Propylene Carbonate + Dimethoxyethane Mixtures from 25 to 125 °C. *J. Chem. Eng. Data* **2000**, *45*, 1007–1011.

- (18) Reichardt, C.; Welton, T. *Solvents and Solvent Effects in Organic Chemistry*, 4th, Updated and Enlarged ed.; Wiley-VCH: Weinheim, 2011.
- (19) Wu, J.; Lan, Z.; Lin, J.; Huang, M.; Hao, S.; Fang, L. Influence of Solvent on the Poly (acrylic acid)-oligo-(ethylene glycol) Polymer Gel Electrolyte and the Performance of Quasi-Solid-State Dye-Sensitized Solar Cells. *Electrochim. Acta* **2007**, *52*, 7128–7135.
- (20) Zafarani-Moattar, M. T.; Majdan-Cegincara, R. Viscosity, Density, Speed of Sound, and Refractive Index of Binary Mixtures of Organic Solvent + Ionic Liquid, 1-Butyl-3-Methylimidazolium Hexafluorophosphate at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 2359–2364.
- (21) Aparicio, S.; Alcalde, R. Characterization of Two Lactones in Liquid Phase: An Experimental and Computational Approach. *Phys. Chem. Chem. Phys.* **2009**, *11*, 6455–6467.
- (22) Couadou, E.; Jacquemin, J.; Galiano, H.; Hardacre, C.; Anouti, M. A Comparative Study on the Thermophysical Properties for Two Bis[(trifluoromethyl)sulfonyl]imide-Based Ionic Liquids Containing the Trimethyl-Sulfonium or the Trimethyl-Ammonium Cation in Molecular Solvents. *J. Phys. Chem. B* **2013**, *117*, 1389–1402.
- (23) Coadou, E.; Timperman, L.; Jacquemin, J.; Galiano, H.; Hardacre, C.; Anouti, M. Comparative Study on Performances of Trimethyl-Sulfonium and Trimethyl-Ammonium Based Ionic Liquids in Molecular Solvents as Electrolyte for Electrochemical Double Layer Capacitors. *J. Phys. Chem. C* **2013**, *117*, 10315–10325.
- (24) Zhu, Q.; Song, Y.; Zhu, X.; Wang, X. Ionic Liquid-Based Electrolytes for Capacitor Applications. *J. Electroanal. Chem.* **2007**, *601*, 229–236.
- (25) Chagnes, A.; Allouchi, H.; Carre, B.; Lemordant, D. Thermal Analysis of γ -Butyrolactone+1 Butyl-3-Methyl-Imidazolium Ionic Liquids Mixtures. *Solid State Ionics* **2005**, *176*, 1419–1427.
- (26) Chagnes, A.; Diaw, M.; Carré, B.; Willmann, P.; Lemordant, D. Imidazolium-Organic Solvent Mixtures as Electrolytes for Lithium Batteries. *J. Power Sources* **2005**, *145*, 82–88.
- (27) Menjoge, A.; Dixon, J.; Brennecke, J. F.; Maginn, E. J.; Vasenkov, S. Influence of Water on Diffusion in Imidazolium-Based Ionic Liquids: A Pulsed Field Gradient NMR study. *J. Phys. Chem. B* **2009**, *113*, 6353–6359.
- (28) Hou, J.; Zhang, Z.; Madsen, L. A. Cation/Anion Associations in Ionic Liquids Modulated by Hydration and Ionic Medium. *J. Phys. Chem. B* **2011**, *115*, 4576–4582.
- (29) Stark, A.; Zidell, A. W.; Hoffmann, M. M. Is the Ionic Liquid 1-Ethyl-3-Methylimidazolium Methanesulfonate [emim][MeSO₃] Capable of Rigidly Binding Water? *J. Mol. Liq.* **2011**, *160*, 166–179.
- (30) Rollet, A.-L.; Porion, P.; Vaultier, M.; Billard, I.; Deschamps, M.; Bessada, C.; Jouvencal, L. Anomalous Diffusion of Water in [BMIM][TFSI] Room-Temperature Ionic Liquid. *J. Phys. Chem. B* **2007**, *111*, 11888–11891.
- (31) Hall, C. A.; Le, K. A.; Rudaz, C.; Radhi, A.; Lovell, C. S.; Damion, R. A.; Budtova, T.; Ries, M. E. Macroscopic and Microscopic Study of 1-Ethyl-3-methyl-imidazolium Acetate–Water Mixtures. *J. Phys. Chem. B* **2012**, *116*, 12810–12818.
- (32) Stark, A.; Zidell, A. W.; Russo, J. W.; Hoffmann, M. M. Composition Dependent Physicochemical Property Data for the Binary System Water and the Ionic Liquid 1-Butyl-3-methylimidazolium Methanesulfonate ([C₄mim][MeSO₃]). *J. Chem. Eng. Data* **2012**, *57*, 3330–3339.
- (33) Cornellas, A.; Perez, L.; Comelles, F.; Ribosa, I.; Manresa, A.; Garcia, M. T. Self-Aggregation and Antimicrobial Activity of Imidazolium and Pyridinium Based Ionic Liquids in Aqueous Solution. *J. Colloid Interface Sci.* **2011**, *355*, 164–171.
- (34) Seddon, K. R.; Stark, A.; Torres, M.-J. Influence of Chloride, Water, and Organic Solvents on the Physical Properties of Ionic Liquids. *Pure Appl. Chem.* **2000**, *72*, 2275–2287.
- (35) Umecky, T.; Kanakubo, M.; Ikushima, Y. Self-Diffusion Coefficients of 1-Butyl-3-Methylimidazolium Hexafluorophosphate with Pulsed-Field Gradient Spin-Echo NMR Technique. *Fluid Phase Equilib.* **2005**, *228–229*, 329–333.
- (36) Umecky, T.; Takamuku, T.; Matsumoto, T.; Kawai, E.; Takagi, M.; Funazukuri, T. Effects of Dissolved Water on Li⁺ Solvation in 1-Ethyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)amide Ionic Liquid Studied by NMR. *J. Phys. Chem. B* **2013**, *117*, 16219–16226.
- (37) Yangzhong, L. *NMR Temperature Calibration*. http://staff.ustc.edu.cn/~liuyz/methods/NMR_VT_calibration.htm (accessed Jan 30, 2014).
- (38) Wu, D. H.; Chen, A. D.; Johnson, C. S. An Improved Diffusion-Ordered Spectroscopy Experiment Incorporating Bipolar-Gradient Pulses. *J. Magn. Reson., Ser. A* **1995**, *115*, 260–264.
- (39) Esturau, N.; Sánchez-Ferrando, F.; Gavin, J. A.; Roumestand, C.; Delsuc, M.-A.; Parella, T. The Use of Sample Rotation for Minimizing Convection Effects in Self-Diffusion NMR Measurements. *J. Magn. Reson.* **2001**, *153*, 48–55.
- (40) Augé, S.; Amblard-Blondel, B.; Delsuc, M.-A. Investigation of the Diffusion Measurement Using PFG and Test of Robustness against Experimental Conditions and Parameters. *J. Chim. Phys. Phys.-Chim. Biol.* **1999**, *96*, 1559–1565.
- (41) Annat, G.; MacFarlane, D. R.; Forsyth, M. Transport Properties in Ionic Liquids and Ionic Liquid Mixtures: The Challenges of NMR Pulsed Field Gradient Diffusion Measurements. *J. Phys. Chem. B* **2007**, *111*, 9018–9024.
- (42) Longworth, L. G. The Mutual Diffusion of Light and Heavy Water. *J. Phys. Chem.* **1960**, *64*, 1914–1917.
- (43) Tanner, J. E.; Stejskal, E. O. Restricted Self-Diffusion of Protons in Colloidal Systems by the Pulsed-Gradient, Spin-Echo Method. *J. Chem. Phys.* **1968**, *49*, 1768–1777.
- (44) Liang, M.; Zhang, X.-X.; Kaintz, A.; Ernsting, N. P.; Maroncelli, M. Solvation Dynamics in a Prototypical Ionic Liquid + Dipolar Aprotic Liquid Mixture: 1-Butyl-3-methylimidazolium Tetrafluoroborate + Acetonitrile. *J. Phys. Chem. B* **2014**, *118*, 1340–1352.
- (45) Hurler, R. L.; Woolf, L. A. Self-Diffusion in Liquid Acetonitrile under Pressure. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2233–2238.
- (46) Holz, M.; Mao, X.-a.; Seiferling, D.; Sacco, A. Experimental Study of Dynamic Isotope Effects in Molecular Liquids: Detection of Translation-Rotation Coupling. *J. Chem. Phys.* **1996**, *104*, 669–679.
- (47) Hawlicka, E.; Grabowski, R. Solvation of Ions in Acetonitrile-Methanol Solutions of Sodium Iodide. *Berichte der Bunsengesellschaft für physikalische Chemie* **1990**, *94*, 486–489.
- (48) Aihara, Y.; Sugimoto, K.; Price, W. S.; Hayamizu, K. Ionic Conduction and Self-Diffusion Near Infinitesimal Concentration in Lithium Salt-Organic Solvent Electrolytes. *J. Chem. Phys.* **2000**, *113*, 1981–1991.
- (49) Hayamizu, K.; Aihara, Y.; Arai, S.; Garcia, Pulse-Gradient Spin-Echo ¹H, ⁷Li, and ¹⁹F NMR Diffusion and Ionic Conductivity Measurements of 14 Organic Electrolytes Containing LiN(SO₂CF₃)₂. *J. Phys. Chem. B* **1999**, *103*, 519–524.
- (50) Hayamizu, K.; Aihara, Y.; Arai, S.; Price, W. S. Diffusion, Conductivity and DSC Studies of a Polymer Gel Electrolyte Composed of Cross-Linked PEO, γ -Butyrolactone and LiBF₄. *Solid State Ionics* **1998**, *107*, 1–12.
- (51) Takeuchi, M.; Kameda, Y.; Umebayashi, Y.; Ogawa, S.; Sonoda, T.; Ishiguro, S.-i.; Fujita, M.; Sano, M. Ion–Ion Interactions of LiPF₆ and LiBF₄ in Propylene Carbonate Solutions. *J. Mol. Liq.* **2009**, *148*, 99–108.
- (52) Kondo, K.; Sano, M.; Hiwara, A.; Omi, T.; Fujita, M.; Kuwae, A.; Iida, M.; Mogi, K.; Yokoyama, H. Conductivity and Solvation of Li⁺ Ions of LiPF₆ in Propylene Carbonate Solutions. *J. Phys. Chem. B* **2000**, *104*, 5040–5044.
- (53) Tsunekawa, H.; Narumi, A.; Sano, M.; Hiwara, A.; Fujita, M.; Yokoyama, H. Solvation and Ion Association Studies of LiBF₄–Propylenecarbonate and LiBF₄–Propylenecarbonate–Trimethyl Phosphate Solutions. *J. Phys. Chem. B* **2003**, *107*, 10962–10966.
- (54) Nama, D.; Kumar, P.; Pregosin, P.; Geldbach, T.; Dyson, P. ¹H, ¹⁹F-HOESY and PGSE Diffusion Studies on Ionic Liquids: The Effect of Co-Solvent on Structure. *Inorg. Chim. Acta* **2006**, *359*, 1907–1911.
- (55) Wu, T.-Y.; Wang, H.-C.; Su, S.-G.; Gung, S.-T.; Lin, M.-W.; Lin, C.-B. Aggregation Influence of Polyethyleneglycol Organic Solvents

with Ionic Liquids BMIMBF₄ and BMIPF₆. *J. Chin. Chem. Soc.* **2010**, *57*, 44–55.

(56) Hawlicka, E. Self-Diffusion in Multicomponent Liquid Systems. *Chem. Soc. Rev.* **1995**, *24*, 367–377.

(57) Scharf, N. T.; Stark, A.; Hoffmann, M. M. Ion Pairing and Dynamics of the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis-(trifluoromethylsulfonyl)amide ([C₆mim][NTf₂]) in the Low Dielectric Solvent Chloroform. *J. Phys. Chem. B* **2012**, *116*, 11488–11497.

(58) Hsu, W.-Y.; Tai, C.-C.; Su, W.-L.; Chang, C.-H.; Wang, S.-P.; Sun, I. W. A Criterion for Proper Cosolvents Used for Ionic Liquids: the Lewis Acidic and Basic Dual Nature of Propylene Carbonate. *Inorg. Chim. Acta* **2008**, *361*, 1281–1290.

(59) Hayamizu, K. Temperature Dependence of Self-Diffusion Coefficients of Ions and Solvents in Ethylene Carbonate, Propylene Carbonate, and Diethyl Carbonate Single Solutions and Ethylene Carbonate + Diethyl Carbonate Binary Solutions of LiPF₆ Studied by NMR. *J. Chem. Eng. Data* **2012**, *57*, 2012–2017.

(60) Hayamizu, K.; Matsuo, A.; Arai, J. A Divalent Lithium Salt Li₂B₁₂F₁₂ Dissolved in Propylene Carbonate Studied by NMR Methods. *J. Electrochem. Soc.* **2009**, *156*, A744–A750.

(61) Hayamizu, K.; Aihara, Y. Ion and Solvent Diffusion and Ion Conduction of PC-DEC and PC-DME Binary Solvent Electrolytes of LiN(SO₂CF₃)₂. *Electrochim. Acta* **2004**, *49*, 3397–3402.

(62) Aihara, Y.; Bando, T.; Nakagawa, H.; Yoshida, H.; Hayamizu, K.; Akiba, E.; Price, W. S. Ion Transport Properties of Six Lithium Salts Dissolved in γ -Butyrolactone Studied by Self-Diffusion and Ionic Conductivity Measurements. *J. Electrochem. Soc.* **2004**, *151*, A119–A122.

(63) Alam, T. M.; Dreyer, D. R.; Bielawski, C. W.; Ruoff, R. S. Combined Measurement of Translational and Rotational Diffusion in Quaternary Acyclic Ammonium and Cyclic Pyrrolidinium Ionic Liquids. *J. Phys. Chem. B* **2013**, *117*, 1967–1977.

(64) Hayamizu, K.; Tsuzuki, S.; Seki, S.; Umebayashi, Y. Multinuclear NMR Studies on Translational and Rotational Motion for Two Ionic Liquids Composed of BF₄ Anion. *J. Phys. Chem. B* **2012**, *116*, 11284–11291.

(65) Taylor, A. W.; Licence, P.; Abbott, A. P. Non-Classical Diffusion in Ionic Liquids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 10147–10154.

(66) Durand, J.; Fernández, F.; Barrière, C.; Teuma, E.; Gómez, K.; González, G.; Gómez, M. DOSY Technique Applied to Palladium Nanoparticles in Ionic Liquids. *Magn. Reson. Chem.* **2008**, *46*, 739–743.

(67) Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D. Determining Accurate Molecular Sizes in Solution through NMR Diffusion Spectroscopy. *Chem. Soc. Rev.* **2008**, *37*, 479.

(68) McLaughlin, E. Viscosity and Self-Diffusion in Liquids. *Trans. Faraday Soc.* **1959**, *55*, 28–38.

(69) Einstein, A. *Investigations on the Theory of the Brownian Movement*; Dover Publications: New York, 1956; pp 68–85.

(70) Wu, T.-Y.; Wang, H.-C.; Su, S.-G.; Gung, S.-T.; Lin, M.-W.; Lin, C.-b. Characterization of Ionic Conductivity, Viscosity, Density, and Self-Diffusion Coefficient for Binary Mixtures of Polyethyleneglycol (or Polyethyleneimine) Organic Solvent with Room Temperature Ionic Liquid BMIBF₄ (or BMIPF₆). *J. Taiwan Inst. Chem. Eng.* **2010**, *41*, 315–325.

(71) Scharf, N.; Stark, A.; Hoffmann, M. Calorimetric Study on the Ion Pairing and Aggregation of 1-Ethyl-3-Methylimidazolium bis(trifluoromethylsulfonyl)amide ([C₂mim][NTf₂]) and Related Ionic Liquids in the Low-Dielectric Constant Solvent Chloroform. *J. Solution Chem.* **2013**, *42*, 2034–2056.

(72) Chen, W.-T.; Hsu, W.-Y.; Lin, M.-Y.; Tai, C.-C.; Wang, S.-P.; Sun, I. W. Isolated BMI⁺ Cations Are More than Isolated PF₆[−] Anions in the Room Temperature 1-Butyl-3-Methylimidazolium Hexafluorophosphate (BMI-PF₆) Ionic Liquid. *J. Chin. Chem. Soc.* **2010**, *57*, 1293–1298.

(73) Urahata, S. M.; Ribeiro, M. C. C. Single Particle Dynamics in Ionic Liquids of 1-Alkyl-3-Methylimidazolium Cations. *J. Chem. Phys.* **2005**, *122* (024511), 1–9.

(74) Chaban, V. Polarizability versus Mobility: Atomistic Force Field for Ionic Liquids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 16055–16062.

(75) Chaban, V. V.; Voroshylova, I. V.; Kalugin, O. N.; Prezhdo, O. V. Acetonitrile Boosts Conductivity of Imidazolium Ionic Liquids. *J. Phys. Chem. B* **2012**, *116*, 7719–7727.

(76) Liu, H.; Maginn, E. A Molecular Dynamics Investigation of the Structural and Dynamic Properties of the Ionic Liquid 1-n-Butyl-3-Methylimidazolium Bis(Trifluoromethanesulfonyl)Imide. *J. Chem. Phys.* **2011**, *135* (124507), 1–16.