Enhanced Lithium Transference Numbers in Ionic Liquid Electrolytes

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Ion transport processes in mixtures of *N*-butyl-*N*-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI) and lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) were characterized by ac impedance spectroscopy and pulsed field gradient NMR. Molar ratios $x = n_{\text{Li-TFSI}}/(n_{\text{Li-TFSI}} + n_{\text{BMP-TFSI}})$ up to 0.377 could be achieved without crystallization. From the bulk ionic conductivity and the individual diffusion coefficients of cations and anions we calculate the Haven ratio and the apparent lithium transference number. Although the Haven ratio exhibits typical values for ionic liquid electrolytes, the maximal apparent lithium transference number is higher than found in other recent studies on ionic liquid electrolytes containing lithium ions. On the basis of these results we discuss strategies for further improving the lithium transference number of such electrolytes.

1. Introduction

Ionic liquid based electrolytes for electrochemical storage and conversion applications offer many advantages over conventional liquid electrolytes based on organic solvents, in particular high chemical and thermally stability, broad electrochemical stability window, low vapor pressure, and nonflammability.^{1,2} The ionic conductivity of ionic liquids at room temperature is generally of the order of $10^{-3}-10^{-2}$ S/cm and thus sufficient for applications as electrolytes.^{1–5} However, the overall ionic conductivity is not the only important transport parameter, but also the individual transference numbers of cations and anions are relevant. For instance, when ionic liquids are used as electrolytes in lithium batteries,⁶ high transference numbers of Li⁺ ions in the electrolyte are needed.

Ion transport and diffusion in ionic liquids consisting of only *one* type of organic cation and *one* type of anion have been studied by means of ac impedance spectroscopy and pulsed field gradient NMR techniques. While the former technique provides information about the overall ionic conductivity, the latter technique allows for the determination of the individual self-diffusion coefficients of cations and anions. Generally, the self-diffusion coefficients of the cations are slightly higher than those of the anions, and the resulting cation transference numbers are typically in the range from 0.5 to 0.65.^{7–10} The Haven ratio calculated from the diffusion coefficients and the overall ionic conductivity is typically in the range from 1.3 to 2, indicating that transport of ion pairs or ion complexes is an important feature.

The situation becomes more complicated when a lithium salt is dissolved in an ionic liquid. In this case, it is recommendable to use a lithium salt containing the same anion as the solvating ionic liquids, since the amount of dissolvable lithium salt is higher than in a mixture with dissimilar anions. Up to now, there are only a few combined ac impedance and pulsed field gradient NMR studies on such systems. Saito et al. have investigated mixtures of 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide (BMI-

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TFSI) with lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) and of 1-butyl-2,3-dimethyl-imidazolium bis(trifluoromethanesulfonyl)imide (BDMI-TSFI) with Li-TFSI.¹¹ The maximum molar ratio $x = n_{\text{Li-TFSI}}/(n_{\text{Li-TFSI}} + n_{B(D)MI-TFSI})$ was about 0.24. Saito et al.¹¹ did not explicitly calculate ionic transference numbers, but their results for the individual diffusion coefficients of Li⁺, BMI⁺, BDMI⁺, and TFSI⁻ ions imply that the maximum Li⁺ transference number at room temperature is below 10%. Similar results have been obtained by Nicotera et al. for mixtures of *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (MPP-TFSI) and Li-TFSI with a maximal molar ratio $x = 0.25^8$ and by Hayamizu et al. for mixtures of 1-ethyl-3-methyl-imidazolium-BF₄ (EMI-BF₄) and Li-BF₄.¹²

Thus, the question arises whether it is possible to improve the Li⁺ transference number by dissolving more lithium salt in ionic liquids. In this paper, we report results for a mixture of *N*-butyl-*N*-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI) and Li-TFSI. Here, molar ratios up to x = 0.377 are obtainable at room temperature without crystallization. We find that, in this system, the achievable Li⁺ transference number is higher than in the mixtures studied in refs 8, 11, and 12. On the basis of our results, we discuss strategies for further enhancements of the Li⁺ transference number.

2. Experimental Section

2.1. Preparation of BMP-TFSI/Li-TFSI Mixtures. BMP-TFSI was purchased from Solvent Innovation, Li-TFSI was from Sigma Aldrich, and dry methanol (max 0.0005% water) was from Riedel-de-Haen. Li-TFSI was dissolved in dry methanol under dry nitrogen gas, and then BMP-TSFI was added. After stirring the solution, the methanol was removed under vacuum, and the resulting BMP-TFSI/Li-TFSI mixture was stirred for 5 h at a temperature of 90 °C and pressure of 2×10^{-4} mbar. Finally, the mixture was stored in a glovebox (MBraun Labstar, <0.1 ppm H₂O, <0.1 ppm O₂).

2.2. Differential Scanning Calorimetry (DSC). A Mettler Toledo DSC/821 was used to detect the heat flow difference

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Figure 1. Illustration of the sample cell used for impedance spectroscopic measurements on ionic liquids.

between a 40 mL aluminum crucible containing the ionic liquid under inert gas atmosphere and a reference aluminum crucible.

2.3. Alternating Current Impedance Measurements. For the ac impedance measurements, a sealed sample cell was constructed, which is illustrated in Figure 1. The Teflon cell consists of two parts which were screwed together in a glovebox (MBraun Labstar, <0.1 ppm H₂O, <0.1 ppm O₂) after the liquid mixtures had been filled in. The lower part contains the sample compartment with two cylindrical brass electrodes, which are connected to the impedance analyzer. Just below the sample compartment there is a small hole for a Pt100 temperature sensor. The upper part contains a gas tap. After carrying out an impedance measurement, the sample cell was evacuated and stored again in a glovebox. This ensured that the liquid mixtures were always kept under protective gas.

The ac impedance measurements were carried out in a frequency range from 0.1 Hz to 1 MHz and at temperatures between 20 and 90 °C using a Novocontrol Alpha-AK impedance analyzer. The analyzer provides an impedance range from 10^{14} to $10^{-2} \Omega$. The rms ac voltage was typically 0.5 V. The sample temperature was controlled by the Novocontrol Quatro cryosystem using dry nitrogen gas.

The geometrical factor of the sample cell, k, was determined by a calibration measurement with a conductance standard solution (specific conductivity $\sigma = 11.67$ mS/cm, Fluka). The geometrical factor was used to calculate the specific ionic conductivity of the ionic liquid from the measured impedances.

2.4. Pulsed Field Gradient NMR Studies. For the ¹H, ⁷Li, and ¹⁹F NMR measurements, a 400 MHz UltraShield 89 mm cryomagnet with a magnetic flux density of B = 9.4 T (Oxford Instruments) in combination with an Avance 400 spectrometer with XWIN-NMR software (Bruker BioSpin) was used. The probe head (Diff30, Bruker) contained gradient coils allowing magnetic field gradients up to 12 T/m. A selective rf insert was used for each of the three nuclei. The ionic liquids were filled into 5 mm NMR tubes, which were sealed. The self-diffusion coefficients *D* were measured by means of the pulsed gradient



Figure 2. (a) DSC trace of a pure BMP-TFSI mixture (x = 0) during a heating experiment with a rate of 10 K/min. (b) DSC traces of ((1 – x)BMP-TFSI)(xLi-TFSI) mixtures with x = 0.233 and 0.377 during a heating experiment with a rate of 10 K/min. (c) DSC traces of ((1 – x)BMP-TFSI)(xLi-TFSI) mixtures with x = 0.233 and 0.377 during a cooling experiment with a rate of 10 K/min.

stimulated echo (PGSTE technique).^{13,14} In this technique, the echo signal I is given by

$$I(\tau, T_{\rm M}, G) = \frac{1}{2}I_0 \exp\left[-\left(\frac{2\tau}{T_2}\right) - \left(\frac{T_{\rm M}}{T_1}\right)\right] \exp\left(-\gamma^2 G^2 \delta^2 D\left(\Delta - \frac{\delta}{3}\right)\right) \quad (1)$$

Here, τ and $T_{\rm M}$ denote the time between the first and the second and between the second and the third 90° pulse, respectively, while T_1 and T_2 are the spin-lattice and spin-spin relaxation Lithium Transference Numbers in Ionic Liquids



Figure 3. (a) Nyquist plot of the ac impedance spectrum of a ((1 - x)BMP-TFSI)(xLi-TFSI) mixture with x = 0.377 at 20 °C. (b) Equivalent circuit for fitting the ac impedance. The bulk impedance of the liquid is represented by bulk resistance R_B , a bulk capacitance C_B , and a constant phase element CPE_B, all acting in parallel. The electrode polarization is described by a constant phase element CPE_{EL} acting in series to the bulk impedance.

times, respectively. G denotes the magnetic field gradient, Δ is the diffusion time, γ is the gyromagnetic ratio, and δ is the duration of the gradient pulse.

In our diffusion experiments, we used $\Delta = 300$ ms and $\delta = 3$ ms. The sample temperature was 20 °C. Intensity data *I*(*G*) were fitted by eq 1 to obtain the diffusion coefficient.

3. Results

3.1. DSC. In Figure 2a we show the DSC trace of pure BMP-TFSI (x = 0) during a heating experiment with a rate of 10 K/min. Above the glass transition temperature ($T_G \approx -84$ °C), the undercooled melt crystallizes at $T_{cryst} \approx -49$ °C and melts again at $T_m \approx -15$ °C. When Li-TFSI is added, the glass transition, the crystallization, and the melting transitions shift to higher temperatures, see Figure 2b. Above 20 °C, all mixtures are molten. During a cooling experiment with a rate of 10 K/min, crystallization processes in the liquids are not detected above -50 °C, see Figure 2c. Thus, when we cool down the sample from higher temperatures, we can study the dynamic processes in the liquids at 20 °C and below without interference from crystallization processes.

3.2. Alternating Current Impedance Measurements. In Figure 3(a) we show a Nyquist plot of the ac impedance of a ((1 - x)BMP-TFSI)(xLi-TFSI) mixture with x = 0.377 at 20 °C. The spectrum consists of a suppressed semicircle, due to ionic conduction in the bulk, and of a low-frequency spike, due to electrode polarization. In order to determine the bulk ionic conductivity, we fitted the spectra using the equivalent circuit shown in Figure 3(b). The bulk impedance of the liquid is represented by a bulk resistance $R_{\rm B}$, a bulk capacitance $C_{\rm B}$, and a constant phase element CPE_B, all acting in parallel. The electrode polarization is described by a constant phase element CPE_{EL} acting in series to the bulk impedance. From the bulk resistance we calculate the bulk ionic dc conductivity $\sigma_{\rm dc} = k/R_{\rm B}$.



Figure 4. Arrhenius plot of the bulk dc conductivity σ_{dc} of the pure BMP-TFSI liquid (x = 0) and of the mixtures with x = 0.233, 0.313, and 0.377.



Figure 5. Bulk dc conductivity σ_{dc} vs Li-TFSI content *x*.

 TABLE 1: Nominal and Experimentally Detected Values of the Compositional Parameter x: Diffusion Coefficients of the Individual Ions from Pulsed Field Gradient NMR

<i>x</i> _{nominal}	X _{NMR}	$x_{\rm NMR}/x_{\rm nominal}$	D _{Li} [cm ² /s]	D _{BMP} [cm ² /s]	D _{TFSI} [cm ² /s]
0				1.31×10^{-7}	1.16×10^{-7}
0.233	0.243 ± 0.012	1.04 ± 0.05	1.43×10^{-8}	3.45×10^{-8}	2.29×10^{-8}
0.313	0.316 ± 0.015	1.01 ± 0.05	7.04×10^{-9}	1.83×10^{-8}	9.09×10^{-9}
0.377	0.385 ± 0.02	1.02 ± 0.05	3.67×10^{-9}	7.32×10^{-9}	4.56×10^{-9}

In Figure 4, we show an Arrhenius plot of σ_{dc} for the pure BMP-TFSI liquid (x = 0) and for the mixtures with x = 0.233, 0.313, and 0.377. The temperature range extends from 20 to 90 °C. Below 10 °C, we find a conductivity drop in the mixtures with x = 0.313and 0.377 due to crystallization processes. The analysis and discussion of these phenomena is, however, beyond the scope of this paper. The data of all liquids shown in Figure 4 exhibit a slightly negative curvature (Vogel–Fulcher–Tamann-type behavior). Furthermore, it is obvious that the overall ionic conductivity decreases with increasing Li-TFSI content of the mixture. In Figure 5, we show a plot of σ_{dc} versus x at 20 °C. For x > 0.1, σ_{dc} decreases, in a good approximation, exponentially with x.

3.3. Pulsed Field Gradient NMR Studies. In Figure 6, we show, as an example, one-dimensional ¹H, ⁷Li, and ¹⁹F NMR spectra of the ((1 - x)BMP-TFSI)(xLi-TFSI) mixture with x = 0.377 at 20 °C. The ⁷Li and ¹⁹F NMR spectra are characterized by a single narrow resonance peak. The integration of these peaks yields the amounts of detectable ⁷Li and ¹⁹F



Figure 6. ¹H, ⁷Li, and ¹⁹F NMR spectra of the mixture with x = 0.377 at 20 °C. In the case of ¹⁹F, the ppm scale was not calibrated.

nuclei in the sample. In order to obtain absolute values, 20% (wt) lithium triflate in D₂O solution was used as standard for ⁷Li and ¹⁹F. In Table 1, we compare the nominal and the detected values of x. Within the experimental error, the values are in good agreement. This indicates that, in contrast to other studies,^{8,15} our liquid mixtures are homogeneous at 20 °C and do not contain crystallites.

In the PGSTE experiments, we observe a linear decay of the normalized area ln I/I_0 with $k = \gamma^2 G^2 \delta^2 (\Delta - \delta/3)$, in agreement with eq 1. In Figure 7, we show, as an example,

such plots for the ¹H, ⁷Li, and ¹⁹F echo decay in the ((1 – *x*)BMP-TFSI)(*x*Li-TFSI) mixture with x = 0.377 at 20 °C. From the slope of the fits, we derive the diffusion coefficients $D_{\rm H} = D_{\rm BMP}$, $D_{\rm Li}$, and $D_{\rm F} = D_{\rm TFSI}$. In Table 1, we list these diffusion coefficients for the pure BMP-TFSI liquid and for the mixtures with x = 0.233, 0.313, and 0.377. Two trends are obvious: (i) The diffusion coefficients of all ionic species decrease with increasing *x*. (ii) For all values of *x*, the diffusion coefficients of the individual ions decrease in the order $D_{\rm BMP} > D_{\rm TFSI} > D_{\rm Li}$.



Figure 7. ¹H (open triangles), ⁷Li (open squares), and ¹⁹F (open circles) echo intensity decay for the mixture with x = 0.377 at 20 °C. Monoexponential fits according to eq 1 are given by the solid, dashed, and dotted lines, respectively.

 TABLE 2: Haven Ratio and Apparent Transference

 Numbers of the Individual Ions

$x_{nominal}$	$H_{\rm R}$	$t_{\rm Li}$	$t_{\rm BMP}$	t _{TFSI}
0	1.41		0.53	0.47
0.233	1.71	0.064	0.50	0.44
0.313	2.00	0.092	0.53	0.38
0.377	1.6	0.132	0.43	0.43

4. Discussion

The relation between the overall ionic conductivity of the liquid mixtures, σ_{dc} , and the individual diffusion coefficients of the ions, D_i , is given by the Nernst–Einstein equation:

$$\sigma_{\rm dc} = \frac{e^2}{k_{\rm B}TH_{\rm R}} [(N_{\rm V,Li^+})(D_{\rm Li^+}) + (N_{\rm V,BMP^+})(D_{\rm BMP^+}) + (N_{\rm V,TFSI^+})(D_{\rm TFSI^-})](2)$$

Here, *e* and $k_{\rm B}$ denote the elementary charge and Boltzmann's constant, respectively, while $N_{\rm V,i}$ are the individual number densities of the ions. The Haven ratio, $H_{\rm R}$, accounts for cross correlations between the movements of different types of ions.

As mentioned in the Introduction, simple ionic liquids with only one type of cation and anion are characterized by Haven ratios typically in the range from 1.3 to 2.0.⁹ A Haven ratio larger than unity indicates that ions of dissimilar charge move preferentially into the same direction, i.e., that transport of ion pairs is relevant. Evidence for such ion pairs was also found in the Raman spectra of ionic liquids.^{15–17} In Table 2, we list values for the Haven ratios for our mixtures. H_R is in the range from 1.6 to 2.0 and does not show a clear compositional trend. The slightly higher H_R values as compared to the ionic liquid with x = 0 indicate that pair formation is more prominent in the mixtures.

As shown in Figure 5, the overall ionic conductivity of the mixtures decreases with increasing lithium salt content x. This conductivity drop is directly related to a drop of the individual self-diffusion coefficients of all ions, see Table 1. Furthermore, studies on different mixtures of ionic liquids with lithium salts have shown that the viscosity increases with increasing lithium salt content x.¹² These findings suggest that the addition of lithium salt leads to stronger ionic bonds in the liquid mixture, which slow down the liquid dynamics. This is plausible, since

the Coulomb interaction between the small lithium ions and the anions should be stronger than the Coulomb interactions between the larger organic cations and the anions. Thus, the decrease of the ionic conductivity with increasing lithium salt content *x* is obviously *not* related to a decreasing number density of mobile ions, but to a decreasing mobility of the ions.

In order to analyze the individual contributions of the cations and anions to the overall ionic conductivity of the mixtures, we define apparent transference numbers t_i by

$$t_i = \frac{N_{\mathrm{V},i}D_i}{\sum_i N_{\mathrm{V},i}D_i} \tag{3}$$

Since all ions are monovalent, individual charges do not have to be taken into account. The apparent transference numbers of Li, BMP, and TFSI are listed in Table 2. The most obvious trend is the increase of the apparent lithium transference number $t_{\rm Li}$ with increasing Li-TFSI content. At x = 0.377, we find $t_{\rm Li}$ = 0.132. We note that this value is clearly higher than the highest t_{Li} values found in other recent studies.^{8,11,12} For a BDMI-TFSI/Li-TFSI mixture with x = 0.244, Saito et al. observe that $D_{\rm Li} \approx 0.3 D_{\rm TFSI}$ and $D_{\rm BDMI} \approx 2.1 D_{\rm TFSI}$ at room temperature.¹¹ This results in $t_{Li} \approx 0.027$. For a BMI-TFSI/Li-TFSI mixture with x = 0.238, they find $D_{\text{Li}} \approx D_{\text{TFSI}}$ and D_{BDMI} $\approx 1.9 D_{\rm TFSI}$ at room temperature, resulting in $t_{\rm Li} \approx 0.09$. Hayamizu et al. find a maximal transference number of $t_{\rm Li} \approx$ 0.045 in EMI-BF4/Li-BF4 mixtures.12 In our BMP-TFSI/Li-TFSI mixture with the highest Li-TFSI content, x = 0.377, we find $D_{\rm Li} \approx 0.8 D_{\rm TFSI}$ and $D_{\rm BMP} \approx 1.6 D_{\rm TFSI}$. This implies that the main reason for the higher apparent lithium transference number in our mixture is the higher number density of lithium ions as compared to other recent studies.

In order to further enhance the lithium transference number in such mixtures, the number density and the diffusion coefficient of the lithium ions have to be further increased with respect to the other ions. A further increase of the number density is not a trivial task, since the mixtures tend to crystallize at high Li salt contents.^{8,15} In order to suppress crystallization, it will be important to choose ionic liquids with cations and anions of low symmetry. For instance, cations with longer alkyl groups should be favorable. Although Nicotera et al. find crystallization at room temperature in mixtures with *N*-methyl-*N*-propyl-pyrrolidinium cations and with x > 0.25,⁸ our mixtures with *N*-methyl-*N*-butyl-pyrrolidinium cations do not crystallize under the same conditions.

The diffusion coefficients of the ions observed in the pulsed field gradient NMR (PFG-NMR) experiments depends on the effective radius of the diffusing entities. Due to the strong interactions between Li⁺ ions and TFSI⁻ ions, Li⁺ ions form $[\text{Li}(\text{TFSI})_{n+1}]^{n-}$ complexes.¹¹ Coordination numbers up to n + 1 = 4 have been reported.^{11,15,17,18} The coordination number determines the effective hydrodynamic radius of the complex and thus the diffusion coefficient in the liquid mixture. Several authors have used the Stokes-Einstein equation

$$D_i = \frac{k_{\rm B}T}{c\pi\eta r_i} \tag{4}$$

in order to calculate an effective hydrodynamic radius of a diffusing entity, r_i , from its diffusion coefficient D_i .^{5,9} The constant *c* varies between 4 and 6, depending on the shape of the diffusing entity. A comparison of the effective hydrodynamic radii of cations and anions in ionic liquids with their van der Waals radii reveals that the *c* values for cations are generally lower than for anions.⁹ In the case of EMI-TFSI/Li-TFSI

mixtures, Umecky et al. found hydrodynamic radii for Li in the range of 0.7–0.9 nm.⁵ This is approximately the van der Waals radius of [Li(TFSI)₂]⁻ and [Li(TFSI)₃]²⁻ complexes. In the case of our BMP-TFSI/Li-TFSI mixture with x = 0.377, the effective hydrodynamic radius of the diffusing lithium complex is $r_{\text{Li}} = (D_{\text{BMP}}/D_{\text{Li}})r_{\text{BMP}} \approx 1.1$ nm, under the assumption that $r_{\rm BMP} \approx 0.55 \text{ nm}^{19}$ and that the *c* values for BMP⁺ and for the diffusing Li complex are identical. This value for $r_{\rm Li}$ suggests that the lithium coordination number in the diffusing complex is at least 2. Since the number of TFSI⁻ ions is not high enough to form a significant amount of $[Li(TFSI)_3]^{2-1}$ complexes, most lithium ions should be diffusing in [Li(TFSI)2]⁻ complexes. If, on the other hand, higher Li salt concentrations were achievable without crystallization, then the mixtures should contain a considerable amount of neutral [Li(TFSI)] complexes, which are smaller ($r_{[\text{Li(TFSI)}]} \approx 0.4 \text{ nm}$) and should have higher diffusivities. Thus, a higher salt concentration would not only enhance the number density of lithium ions but should also lead to higher diffusion coefficients of the diffusing lithium complexes relative to the organic cations.

A second possible strategy is the usage of ionic liquids with larger organic cations. These cations should have lower diffusion coefficients relative to those of the lithium complexes, leading to a higher apparent lithium transference number. Finally, a third strategy is the usage of anions with a lower tendency for lithium coordination, for instance, anions with large aromatic groups, leading to delocalization of the negative charge. This should result in lower coordination numbers of lithium ions in the diffusing complexes and in higher lithium diffusivities.

5. Conclusions

We have studied electrical transport and diffusion processes in BMP-TFSI/Li-TFSI mixtures with different Li-TFSI contents x. Both the ionic conductivity σ_{dc} of the mixtures and the individual diffusion coefficients of the cations and anions decrease with increasing x. The Haven ratio of the mixtures exhibits values between 1.6 and 2.0, which is typical for ionic liquids and points to the transport of ion pairs. The apparent lithium transference number t_{Li} obtained from the individual diffusion coefficients increases with increasing x, and at high values of x, we find t_{Li} values exceeding those previously reported in the literature. The main reason for this is the higher number density of Li⁺ ions in our mixtures.

On the basis of these results we have discussed strategies for further improving the lithium transference number. Possible strategies are the following: (i) A further increase of the lithium salt content could be achievable, when crystallization is suppressed by taking organic cations and anions of low symmetry. (ii) Bigger organic cations should have a lower diffusion coefficient relative to the diffusing lithium complexes. (iii) Less lithium-coordinating anions should lead to lower coordination numbers of lithium in the diffusing complexes and thus to higher lithium diffusivities.

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