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# Electrolytic conductivity of four imidazolium-based room-temperature ionic liquids and the effect of a water impurity

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## Abstract

The electrolytic conductivities ( $\kappa$ ) of four hydrophobic room-temperature ionic liquids (RTILs) were measured at temperatures from (288.15 to 323.15) K. The measurements were made with a commercial conductivity cell with platinum black electrodes. In order to exclude atmospheric moisture, the conductivity cell was modified so that it could be sealed during measurements. The RTILs studied were 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and 1-butyl-3-methylimidazolium hexafluorophosphate. The RTILs were dried under vacuum until the mass fraction of water ( $w_{H_2O}$ ) was  $\leq 10^{-5}$ . Coulometric Karl Fischer titration was used to determine  $w_{H_2O}$  in each RTIL before and after measurements of  $\kappa$ . Most measurements were made on dried RTILs, but some measurements were performed intentionally at higher  $w_{H_2O}$  in order to study the effect of a water impurity on  $\kappa$ . For {water + 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide},  $\kappa$  was found to increase dramatically with increasing  $w_{H_2O}$ ; for example, in going from  $w_{H_2O} = 10^{-5}$  to  $10^{-2}$ , the fractional increase in  $\kappa$  was 0.36 {=( $\kappa_{wet} - \kappa_{dried}$ )/ $\kappa_{dried}$ }. This work illustrates the importance of measuring the water content in RTILs both before and after measurements of  $\kappa$ .

Keywords: Electrolytic conductivity; Room-temperature ionic liquid; Room-temperature molten salt; Specific conductance; Water impurity

#### 1. Introduction

Room-temperature ionic liquids (RTILs) are salts that melt at or below room temperature [1]. One inherent difference between RTILs and conventional molecular liquids is that RTILs exhibit high electrolytic conductivity,  $\kappa$  (formerly called specific conductance or ionic conductivity). They also have a variety of other potentially useful properties, including excellent electrochemical and thermal stability, negligible vapor pressure, and a wide liquid range [2–4]. As a result, RTILs have attracted a great deal of attention for their potential use in electrochemical devices such as capacitors, dye-sensitized solar cells, batteries, and fuel cells.

When selecting an RTIL for an electrochemical use,  $\kappa$  is of critical importance [2]. One impediment to the use of RTILs is the shortage of reliable data for  $\kappa$  [2,5]. For many RTILs, little or no data have been published. An example of such a case is 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, abbreviated herein as [C<sub>6</sub>mim][Tf<sub>2</sub>N], for which the only available data are at (295 ± 2) K [6]. For other RTILs, extensive, but inconsistent, data have been published. An example of such a case is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>2</sub>mim][Tf<sub>2</sub>N], for which

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several groups have reported values of  $\kappa$  in the temperature range (263 to 401) K [7–14]. Unfortunately, the data sets for [C<sub>2</sub>mim][Tf<sub>2</sub>N] are in poor agreement, as illustrated by the published values of  $\kappa$  at 293 K: 0.49 S · m<sup>-1</sup> (from a correlation) [10], 0.77 S · m<sup>-1</sup> (estimated from a graph) [12], 0.82 S · m<sup>-1</sup> (estimated from a graph) [7], 0.88 S · m<sup>-1</sup> [14], and 0.99 S · m<sup>-1</sup> [8,11].

Inconsistent sample purity is a likely reason for much of the disagreement in the reported values of  $\kappa$  for RTILs [2]. Water is arguably the most important impurity to consider for four reasons. First, atmospheric moisture is ubiquitous. Second, even "hydrophobic" RTILs, which are not miscible with water, rapidly absorb water from the atmosphere [15-18] or from moist surfaces. Hence, unless an RTIL is carefully dried and handled, it will be contaminated with water. Third, some data already exist that show that the presence of water increases  $\kappa$  in (RTIL + water) [6,19,20]. Fourth, literature reports regarding the viscosity  $(\eta)$  of (RTIL + water) suggest that even trace levels of water could significantly increase  $\kappa$  by lowering  $\eta$  [21,22]. That work showed that a mass fraction of water  $(w_{\rm H_2O})$  of only  $10^{-4}$  can significantly lower  $\eta$  in (RTIL + water) [21]. According to the Walden Rule [2,23], the molar conductivity (A) is inversely proportional to  $\eta$ ,

$$\Lambda \cdot \eta = \text{constant},\tag{1}$$

where  $\Lambda = \kappa/c$ , and *c* is the amount of substance concentration. Hence, on the basis of the Walden Rule, we predict that trace amounts of water will significantly increase  $\kappa$  in (RTIL + water).

The first aim of this work was to measure  $\kappa$  as a function of temperature for RTILs of known high purity, especially with respect to water content. The second aim of this work was assess the effect of small amounts of water on  $\kappa$  in (RTIL + water). A key to these experiments was that coulometric Karl Fischer titration was used to determine  $w_{H_{2}O}$  both before *and after* measurements of  $\kappa$  [21].

The RTILs chosen for this study are based on the 1-nalkyl-3-methylimidazolium cation, abbreviated herein as  $[C_i \text{mim}]^+$ , where *i* equals the number of carbons in the *n*alkyl side chain. This class of cations is widely used because it results in RTILs with relatively low viscosities and relatively high thermal stabilities. The primary anion chosen for this study is bis(trifluoromethylsulfonyl)imide,  $[(F_3CSO_2)_2N]^-$ , abbreviated herein as  $[Tf_2N]^-$ . This anion is widely used because it results in RTILs with relatively low viscosities, and it has good hydrolytic and electrochemical stability [14]. One RTIL containing the hexafluorophosphate anion,  $[PF_6]^-$ , was included in this study for the purposes of comparison. In all,  $\kappa$  was measured for four RTILs: [C<sub>2</sub>mim][Tf<sub>2</sub>N],  $[C_4 mim][Tf_2N]$ ,  $[C_6 mim][Tf_2N]$ , and  $[C_4 mim][PF_6]$ . Additionally,  $\kappa$  was measured for mixtures of  $[C_4 mim][Tf_2N]$  and water.

# 2. Experimental

#### 2.1. Materials

The  $[C_2 mim][Tf_2N],$  $[C_4 mim][Tf_2N],$ and  $[C_4 mim][PF_6]$  were commercially obtained. The [C<sub>6</sub>mim][Tf<sub>2</sub>N] was synthesized by Dr. Mark Muldoon at the University of Notre Dame using the following procedure. First, 1-methylimidazole (mole fraction x = 0.476) was mixed with a small excess of 1-bromohexane (x = 0.524) at room temperature in a roundbottom flask fitted with a condenser and  $N_2$  bubbler. After (30 to 45) min the clear mixture started to become cloudy, at which point the flask was placed in an ice bath and left to stir overnight. The reaction mixture was then heated at 343 K for 8 h, resulting in complete conversion of 1-methylimidazole to 1-hexyl-3-methylimidazolium bromide. The bromide salt was then washed with dry ethyl acetate several times to remove the excess 1bromohexane. The residual ethyl acetate was removed under reduced pressure at 323 K. Then the 1-hexyl-3methylimidazolium bromide (x = 0.476) was mixed with a small excess of lithium bis(trifluoromethylsulfonyl)imide (x = 0.524) by dissolving each in deionized water and combining the solutions. This mixture was stirred for 3 h, the product forming a separate phase below the aqueous solution. To ensure the removal of the excess lithium bis(trifluoromethylsulfonyl)imide and the LiBr byproduct, the water-immiscible  $[C_6 mim][Tf_2N]$ was washed with deionized water until the water phase no longer gave a precipitate upon addition of a silver nitrate solution. As a precaution, the  $[C_6 mim][Tf_2N]$  was then washed several more times with deionized water to ensure that the last traces of the water-soluble salts were removed. At this point, the  $[C_6 mim][Tf_2N]$  was dried under vacuum at 333 K to remove the residual water. Analysis with a commercial bromide-selective electrode showed that the mass fraction of bromide was below the detection limit of the electrode  $(w_{\rm Br} < 10^{-5})$ . To remove traces of color and other impurities, the [C<sub>6</sub>mim][Tf<sub>2</sub>N] was then dissolved in dichloromethane and stirred overnight with activated carbon at 343 K before being passed through a column of activated alumina (60% acidic, 20% basic, and 20% neutral). The dichloromethane was then removed under reduced pressure.

All four RTILs were dried thoroughly before being used for conductivity measurements. The drying was done at room temperature with stirring on a vacuum line using a mechanical pump and a liquid nitrogen trap; the ultimate pressure during drying was  $\leq 0.1$  Pa. After drying, the RTILs were stored in a nitrogen atmosphere in a glove box. Coulometric Karl Fischer titration indicated that  $w_{H_2O} \leq 10^{-5}$  for all four dried RTILs. For the three commercially obtained RTILs, silver nitrate tests and chloride-selective electrode measurements were used to verify the manufacturer's claim that  $w_{Cl} < 5 \cdot 10^{-5}$ . (The counter ion associated with a chloride impurity is simply the  $[C_i \text{mim}]^+$ .) After drying, the purities of the RTILs were also checked by <sup>1</sup>H and <sup>19</sup>F nuclear magnetic resonance (NMR) spectrometry. To check if contamination or decomposition had occurred during measurements of  $\kappa$ , NMR spectra were also obtained after measuring  $\kappa$ . In every case, the purity of the RTILs was >99.5% by both <sup>1</sup>H and <sup>19</sup>F NMR.

Mixtures of  $([C_4mim][Tf_2N] + water)$  were made by adding deionized water (with a resistivity of  $\ge 18$  $M\Omega \cdot cm$ ) to the dried  $[C_4mim][Tf_2N]$  and stirring. These mixtures were handled in the same manner as the dried RTIL samples.

# 2.2. Apparatus and procedure

The ac impedance bridge technique [2,24,25] was used to measure  $\kappa$  as a function of T at about 0.1 MPa. Measurements were made with a small-volume commercial conductivity cell with a nominal cell constant,  $K_{cell}$  of  $100 \text{ m}^{-1}$ . The cell was made of borosilicate glass with two platinum black electrodes. In order to exclude atmospheric moisture during measurements, the cell was modified so that it could be capped on both ends with O-ring-sealed poly(tetrafluoroethylene) (PTFE) plugs. A small void volume at both ends of the cell (containing  $N_2$  at about 0.1 MPa) assured that the liquid sample did not contact the O-rings or the PTFE plugs. During measurements, the cell was immersed in a constant temperature bath filled with mineral oil. The bath temperature was measured with an ITS-90 calibrated platinum resistance thermometer. The uncertainty in the temperature is estimated to be  $\pm 0.1$  K. To avoid lead resistance effects, the cell was connected via four wires to a commercial precision LCR (inductance, capacitance, and resistance) meter. With this meter, the standard uncertainty in the measurement of electric resistance, *R*, is estimated to be  $u = 5 \cdot 10^{-4} R$ . A drive voltage of  $1.0 V_{\rm rms}$  was used in the C-R series mode for all measurements.

The cell was calibrated at T = 298.15 K using two commercially available conductivity standards (aqueous potassium chloride solutions) with  $\kappa = (0.1 \pm 0.0005)$  $S \cdot m^{-1}$  and  $\kappa = (1.0 \pm 0.0025)$   $S \cdot m^{-1}$  at that temperature. First, *R* at infinite frequency ( $f_{\infty}$ ) was determined by measuring *R* from *f* (0.8 to 5) kHz, then plotting *R* as a function of  $f^{-0.5}$ , and extrapolating the resulting line to  $f_{\infty}$  [25]. For each conductivity standard, the extrapolated value of *R* at  $f_{\infty}$  was then used to calculate the value of  $K_{cell}$  from the equation

$$\kappa = K_{\text{cell}}/R.$$
(2)

Using the (0.1 ± 0.0005) S · m<sup>-1</sup> standard, the value of  $K_{\text{cell}}$  was determined to be (99.8 ± 0.7) m<sup>-1</sup>, and, using the (1.0 ± 0.0025) S · m<sup>-1</sup> standard, the value of  $K_{\text{cell}}$ 

was determined to be  $(100.0 \pm 0.5) \text{ m}^{-1}$ . Since the two values of  $K_{\text{cell}}$  are the same within the estimated uncertainties, we used the average value and assumed the larger uncertainty,  $K_{\text{cell}} = (99.9 \pm 0.7) \text{ m}^{-1}$ .

The conductivity cell was carefully cleaned and dried before each RTIL sample was introduced. The cell was cleaned by soaking and rinsing with ethanol, then with deionized water with a resistivity of  $\geq 18 \text{ M}\Omega \cdot \text{cm}$ . The cell was dried by flowing dry nitrogen through it at room temperature for about 1 h, then placing it under vacuum (uncapped) in the antechamber of the glove box for about 1 h. The cell was then brought into the nitrogen atmosphere glove box and filled with a sample of RTIL. An aliquot of the RTIL sample was then removed from the cell for analysis by coulometric Karl Fischer titration. At this point, the cell was capped, removed from the glove box, and placed in the constanttemperature bath. At each temperature, values of Rwere collected from f = (0.8 to 5) kHz. Then R was plotted as a function of  $f^{-0.5}$  or  $f^{-1}$ , whichever was most linear, and extrapolated to  $f_{\infty}$  [25]. The extrapolated value of R at  $f_{\infty}$  and  $K_{\text{cell}}$  were used to calculate  $\kappa$  from equation (2). Following data collection, the conductivity cell was taken back into the glove box, and aliquots of the RTIL sample were removed from the cell for Karl Fischer and NMR analysis.

Coulometric Karl Fischer titration was carried out in accordance with ASTM Standard Test Method E 1064 -00, except sample sizes of about 1.5 g were used. The values of  $w_{\rm H_2O}$  given herein refer to the average of the values obtained before and after measurements of  $\kappa$ . In general, the value of  $w_{\rm H_{2}O}$  before and after measurements of  $\kappa$ changed by less than the experimental uncertainty in the Karl Fischer measurement. For example, the values of  $w_{\rm H_2O}$  listed in Table 2 are the averages (rounded to the nearest  $1 \cdot 10^{-5}$ ) of the following raw data from Karl  $w_{\rm H_2O, before} = 8.8 \cdot 10^{-6}$ Fischer titrations: and  $w_{\rm H_2O,after} = 8.8 \cdot 10^{-6};$  $w_{\rm H_2O, before} = 8.44 \cdot 10^{-5}$ and  $w_{\text{H}_2\text{O},\text{after}} = 8.02 \cdot 10^{-5};$   $w_{\text{H}_2\text{O},\text{before}} = 1.021 \cdot 10^{-3}$  and  $w_{\text{H}_2\text{O},\text{after}} = 1.019 \cdot 10^{-3};$  and  $w_{\text{H}_2\text{O},\text{before}} = 8.804 \cdot 10^{-3}$ and  $w_{\text{H}_2\text{O},\text{after}} = 8.898 \cdot 10^{-3}$ . Uncertainties in  $w_{\text{H}_2\text{O}}$  were estimated from multiple measurements on commercially available water standards for Karl Fischer titration. Not surprisingly, the uncertainty in  $w_{\rm H_2O}$  changes significantly as a function of the composition. At  $w_{\rm H_2O} = 10^{-2}$ , the expanded uncertainty (with a coverage factor of 2) is estimated to be  $U = 0.04w_{\rm H_2O}$ ; at  $w_{\rm H_2O} = 10^{-3}$ , the expanded uncertainty is estimated to be  $U = 0.06 w_{\text{H}_2\text{O}}$ ; and at  $w_{\text{H}_2\text{O}} = 10^{-4}$ , the expanded uncertainty is estimated to be  $U = 0.2w_{\rm H_2O}$ .

The uncertainty in the bath temperature results in a relative standard uncertainty of  $u_r \leq 8 \cdot 10^{-3}$  in the measurement of  $\kappa$ . The estimated uncertainty in  $K_{\text{cell}}$  results in a relative standard uncertainty of  $u_r = 7 \cdot 10^{-3}$  in the measurement of  $\kappa$ . Based on the results of ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water), the estimated uncertainty in

 $w_{\rm H_{2}O}$  for the dried RTILs results in a relative standard uncertainty of  $u_r = 8 \cdot 10^{-4}$  in the measurement of  $\kappa$ . The estimated uncertainty in the measurement of R with the precision LCR meter results in a relative standard uncertainty of  $u_r = 5 \cdot 10^{-4}$  in the measurement of  $\kappa$ . Hence, using standard techniques for the propagation of uncertainty, the expanded uncertainty (with a coverage factor of 2) in the measurement of  $\kappa$  is  $U = 0.02 \kappa$ .

# 3. Results and discussion

#### 3.1. Electrolytic conductivities of dried RTILs

For each of the four dried RTILs,  $\kappa$  was determined as a function of T at temperatures of (288.15, 293.15, 298.15, 308.15, and 323.15) K using the ac impedance bridge technique (table 1). Special care was taken to control the amount of water present in each RTIL during these measurements, as described in Section 2. Figure 1 shows  $\kappa$  as a function of T for all four RTILs, as well as correlations of the data by quadratic equations (see figure 1 caption for the specific equations). Figure 2 shows the relative deviations of  $\kappa$  from the correlations as a function of T. Figure 2 shows that the quadratic equations do a better job of correlating the data for the [Tf<sub>2</sub>N]-based RTILs, but even the correlation for  $[C_4 mim][PF_6]$  is within the expanded uncertainty of the measurements. For the entire temperature range of (288.15 to 323.15) K, the order of conductivities is  $\kappa_{[C_2\min][Tf_2N]} > \kappa_{[C_4\min][Tf_2N]} > \kappa_{[C_6\min][Tf_2N]} > \kappa_{[C_4\min][PF6]}.$ Figure 1 shows that  $\kappa$  is quite sensitive to the size of the

TABLE 1

Temperature dependence of the electrolytic conductivities ( $\kappa$ ) of dried room-temperature ionic liquids (RTILs)

RTIL	T/K	$\kappa/(\mathbf{S}\cdot\mathbf{m}^{-1})$
[C <sub>2</sub> mim][Tf <sub>2</sub> N]	288.15	0.644
	293.15	0.773
	298.15	0.912
	308.15	1.229
	323.15	1.789
[C <sub>4</sub> mim][Tf <sub>2</sub> N]	288.15	0.265
	293.15	0.331
	298.15	0.406
	308.15	0.585
	323.15	0.924
[C <sub>6</sub> mim][Tf <sub>2</sub> N]	288.15	0.135
	293.15	0.173
	298.15	0.218
	308.15	0.327
	323.15	0.546
[C <sub>4</sub> mim][PF <sub>6</sub> ]	288.15	0.079
	293.15	0.109
	298.15	0.146
	308.15	0.247
	323.15	0.477

The mass fraction of water in these four dried RTILs is  $10^{-5}$ .

## TABLE 2

Electrolytic conductivities ( $\kappa$ ) of ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water) as a function of the mass fraction of water ( $w_{H_{2O}}$ ) and of the temperature

WH <sub>2</sub> O	T/K	$\kappa/(\mathbf{S}\cdot\mathbf{m}^{-1})$	
$1 \cdot 10^{-5}$	288.15	0.265	
$1 \cdot 10^{-5}$	293.15	0.331	
$1 \cdot 10^{-5}$	298.15	0.406	
$8 \cdot 10^{-5}$	288.15	0.266	
$8 \cdot 10^{-5}$	293.15	0.332	
$8 \cdot 10^{-5}$	298.15	0.408	
$1.02\cdot 10^{-3}$	288.15	0.277	
$1.02 \cdot 10^{-3}$	293.15	0.345	
$1.02\cdot 10^{-3}$	298.15	0.422	
$8.85 \cdot 10^{-3}$	288.15	0.365	
$8.85\cdot 10^{-3}$	293.15	0.449	
$8.85 \cdot 10^{-3}$	298.15	0.542	

cation. At 293.15 K, for example,  $(\kappa_{[C_2mim][Tf_2N]} - \kappa_{[C_4mim][Tf_2N]})/\kappa_{[C_2mim][Tf_2N]} = 0.57$ , and  $(\kappa_{[C_4mim][Tf_2N]} - \kappa_{[C_6mim][Tf_2N]})/\kappa_{[C_4mim][Tf_2N]} = 0.48$ . These changes are consistent with a literature report [14] in which it was found that  $(\kappa_{[C_2mim][Tf_2N]} - \kappa_{[C_4mim][Tf_2N]})/\kappa_{[C_2mim][Tf_2N]} = 0.56$  at 293 K. We also find that  $[C_4mim][PF_6]$  has a considerably lower conductivity than  $[C_4mim][Tf_2N] - \kappa_{[C_4mim][Tf_2N]} = 0.56$  at 293.15 K  $(\kappa_{[C_4mim][Tf_2N]} - \kappa_{[C_4mim][Tf_2N]} = 0.67$ .

The relative conductivities of RTILs are typically compared with the Stokes–Einstein relation,

$$D_i = k_{\rm B} T / 6\pi \eta r_i, \tag{3}$$



FIGURE 1. Plot of the electrolytic conductivity ( $\kappa$ ) as a function of temperature for four RTILs. For these dried RTILs the mass fraction of water is  $10^{-5}$ .  $\diamondsuit$ ,  $[C_2 \text{mim}][Tf_2 N]$ , correlated by  $\{\kappa/(\text{S} \cdot \text{m}^{-1})\} = (2.330 \cdot 10^{-4})(T/\text{K})^2 - 0.1097(T/\text{K}) + 12.91; \Box, [C_4 \text{mim}][Tf_2 N]$ , correlated by  $\{\kappa/(\text{S} \cdot \text{m}^{-1})\} = (1.878 \cdot 10^{-4})(T/\text{K})^2 - (9.596 \cdot 10^{-2})(T/\text{K}) + 12.32; \bigcirc$ ,  $[C_6 \text{mim}][Tf_2 N]$ , correlated by  $\{\kappa/(\text{S} \cdot \text{m}^{-1})\} = (1.408 \cdot 10^{-4})(T/\text{K})^2 - (7.435 \cdot 10^{-2})(T/\text{K}) + 9.867; *, [C_4 \text{mim}][PF_6]$ , correlated by  $\{\kappa/(\text{S} \cdot \text{m}^{-1})\} = (1.939 \cdot 10^{-4})(T/\text{K})^2 - 0.1072(T/\text{K}) + 14.86$ .

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FIGURE 2. Plot of the relative deviations of the experimental electrolytic conductivities ( $\kappa_{exp}$ ) from the electrolytic conductivities given by the correlations ( $\kappa_{corr}$ ) in figure 1.  $\Diamond$ , [C<sub>2</sub>mim][Tf<sub>2</sub>N];  $\Box$ , [C<sub>4</sub>mim][Tf<sub>2</sub>N];  $\diamond$ , [C<sub>6</sub>mim][Tf<sub>2</sub>N];  $\star$ , [C<sub>4</sub>mim][PF<sub>6</sub>].

where  $D_i$  is the self-diffusivity of species *i*,  $k_B$  is the Boltzmann constant, T is the temperature,  $\eta$  is the viscosity, and  $r_i$  is the radius of the species *i* [2,23]. In the absence of ion pairing,  $D_i$  is directly proportional to  $\kappa$  [8]. From equation (3) it is easy to rationalize the relative conductivities of  $[C_2 mim][Tf_2N],$  $[C_4 mim][Tf_2N],$ and  $[C_6 mim][Tf_2N]$ . Since  $[C_2 mim][Tf_2N]$  has the smallest cation and the lowest  $\eta$  [14], it is expected to have the largest  $D_i$  and, therefore, the largest  $\kappa$  of the three [Tf<sub>2</sub>N]-based RTILs, which it does. [C<sub>6</sub>mim][Tf<sub>2</sub>N] has the largest cation and the highest  $\eta$ , so it is expected to have the lowest  $\kappa$  of the three [Tf<sub>2</sub>N]-based RTILs, which it does. Predicting the relative conductivity of  $[C_4 mim][PF_6]$  compared to the three  $[Tf_2N]$ -based RTILs is more difficult, since  $[C_4 mim][PF_6]$  has the highest  $\eta$  of the four RTILs studied herein, but it also has the smallest anion. Experimentally we find that the high  $\eta$ has a greater effect than the small anion size because  $[C_4 mim][PF_6]$  has the lowest  $\kappa$  of the four RTILs.

# 3.2. Electrolytic conductivities of $([C_4mim][Tf_2N] + water)$

The viscosity of (RTIL + water) is known to depend strongly on  $w_{H_2O}$  [15,21,22,26,27]. Figure 3, which was constructed from data from reference [21], shows  $\eta$ decreasing rapidly as  $w_{H_2O}$  increases for ([C<sub>4</sub>mim]-[Tf<sub>2</sub>N] + water) at 293.15 K. The data for figure 3 were measured at atmospheric pressure with an Ubbelohde capillary viscometers [21]. The capillaries were open to the atmosphere, but atmospheric moisture was effectively excluded by connecting drying tubes (filled with anhydrous calcium sulfate) to the openings. The water content was determined before and after each viscosity measurement by coulometric Karl Fischer titration.



FIGURE 3. Plot of the viscosities ( $\eta$ ) of ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water) as a function of the mass fraction of water ( $w_{H_{2O}}$ ) at 293.15 K [21].  $\bullet$ , Measured values; —, correlation with the equation  $\{\eta/(\text{Pa} \cdot s)\} = 80.83 \cdot (w_{H_{2O}})^2 - 2.840 \cdot w_{H_{2O}} + 0.06355$ .

Based on the Walden Rule, we expect a decrease in  $\eta$  to be accompanied by an inversely proportional increase in  $\Lambda$ . Furthermore, given the magnitude of the change in  $\eta$  with increasing  $w_{\rm H_2O}$  we expect that even trace levels of water will significantly increase  $\Lambda$  (and, therefore,  $\kappa$ ) of (RTIL + water). To test this prediction we measured  $\kappa$ as a function of  $w_{\rm H_2O}$  for ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water); measurements were made at temperatures of (288.15, 293.15, and 298.15) K and  $w_{\rm H_2O}$  values of  $1 \cdot 10^{-5}$ ,  $8 \cdot 10^{-5}$ ,  $1.02 \cdot 10^{-3}$ , and  $8.85 \cdot 10^{-3}$ . As expected,  $\kappa$  increases dramatically as  $w_{\rm H_2O}$  increases, table 2. Figure 4 shows how



FIGURE 4. Plot of the relative deviations of the electrolytic conductivities ( $\kappa$ ) from the electrolytic conductivities given by the correlation ( $\kappa_{corr}$ ) in figure 1 for dried [C<sub>4</sub>mim][Tf<sub>2</sub>N].  $\diamond$ , ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water) with  $w_{H_2O} = 8.85 \cdot 10^{-3}$ ; \*, ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water) with  $w_{H_2O} = 1.02 \cdot 10^{-3}$ ; +, ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water) with  $w_{H_2O} = 8 \cdot 10^{-5}$ ;  $\bigcirc$ , dried [C<sub>4</sub>mim][Tf<sub>2</sub>N] (for which  $w_{H_2O} = 10^{-5}$ );  $\blacksquare$ , data point from reference [14]; ---, correlation from reference [28].

TABLE 3

WH <sub>2</sub> O	$\kappa/(\mathbf{S}\cdot\mathbf{m}^{-1})$	$100 \cdot (\kappa - \kappa_{\rm dried}) / \kappa_{ m dried}$	$\Lambda/(\mathbf{S}\cdot\mathbf{m}^2\cdot\mathbf{mol}^{-1})^a$	$\Lambda \cdot \eta / \mathbf{S} \cdot \mathbf{kg} \cdot \mathbf{m} \cdot \mathbf{s}^{-1} \cdot \mathbf{mol}^{-1b}$
$1 \cdot 10^{-5}$	0.331	0.0	$9.62 \cdot 10^{-5}$	$6.11 \cdot 10^{-6}$
$8 \cdot 10^{-5}$	0.332	0.4	$9.67 \cdot 10^{-5}$	$6.12 \cdot 10^{-6}$
$1.02 \cdot 10^{-3}$	0.345	4.1	$1.00 \cdot 10^{-4}$	$6.09 \cdot 10^{-6}$
$8.85 \cdot 10^{-3}$	0.449	35.8	$1.31 \cdot 10^{-4}$	$5.85 \cdot 10^{-6}$

Electrolytic conductivities ( $\kappa$ ) of ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water) at 293.15 K, the relative change in  $\kappa$ , the molar conductivity  $\Lambda$ , and the walden, product ( $\Lambda \cdot \eta$ ), all as functions of the and mass fraction of water ( $w_{H_2O}$ )

The molar conductivity ( $\Lambda$ ) and Walden product ( $\Lambda \cdot \eta$ ) are given as a function of  $w_{\rm H_2O}$ .

<sup>*a*</sup> The molar conductivity ( $\Lambda$ ) was calculated using a literature density value [29].

<sup>*b*</sup> Viscosities ( $\eta$ ) were calculated from the correlation given in figure 3.

the conductivity of ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water) deviates from the correlated conductivity data for the dried [C<sub>4</sub>mim][Tf<sub>2</sub>N]. At 293.15 K, for example, ( $\kappa_{exp} - \kappa_{corr}$ )/ $\kappa_{corr} = 0.358$  when the  $w_{H_{2O}} = 8.85 \cdot 10^{-3}$  (table 3). Put another way, increasing  $w_{H_{2O}}$  by only 2.5  $\cdot 10^{-4}$  increases  $\kappa$  by 1%.

Figure 4 includes conductivity data from the literature. For  $[C_4mim][Tf_2N]$ , Bonhôte *et al.* reported [14] that  $\kappa = 0.39 \text{ S} \cdot \text{m}^{-1}$  at 293 K (with an estimated uncertainty of  $U = 0.05 \kappa$ ), which is about 18% higher than the value reported herein for dried  $[C_4mim][Tf_2N]$ . Comparing the literature value of  $\kappa$  to the mixture data reported herein suggests that  $w_{H_2O}$  for the literature sample of  $[C_4mim][Tf_2N]$  was about  $4 \cdot 10^{-3}$ . Figure 4 also shows a portion of the correlation of  $\kappa$  as a function of *T* for  $[C_4mim][Tf_2N]$  that was reported by Watanabe and co-workers [28]. That correlation is lower than the correlation reported herein, but it is not clear if the difference is significant because no estimate of uncertainty was given.

It is of interest to know if the Walden Rule applies to (RTIL + water). Density data are not available for  $([C_4 mim][Tf_2N] + water)$ , but we can still estimate  $\Lambda$ by assuming that the density is not a function of  $w_{\rm H_2O}$ (this assumption is probably correct to within about 1% for these small values of  $w_{\rm H_2O}$  [15]). Hence, the values of  $\Lambda$  in table 3 were calculated from a literature value for the density of [C<sub>4</sub>mim][Tf<sub>2</sub>N] at 293.15 K and 0.1 MPa, 1442.5 kg  $\cdot$  m<sup>-3</sup> [29]. The Walden products  $(\Lambda \cdot \eta)$  shown in table 3 were then calculated from the correlated value of  $\eta$  from figure 3. Over the studied range of compositions,  $\Lambda \cdot \eta$  ranges from  $(6.12 \cdot 10^{-6})$ to  $5.85 \cdot 10^{-6}$ ) S · kg · m · s<sup>-1</sup> · mol<sup>-1</sup>, a change of only about 4% (compared to a 36% change in  $\kappa$ ). This is excellent evidence that the change in  $\eta$  is indeed primarily responsible for the change in  $\kappa$ . The small change in  $\Lambda \cdot \eta$  with increasing  $w_{\rm H_2O}$  could be due to a relatively minor effect (such as a change in the extent of ion pairing with increasing  $w_{\rm H,O}$ ). Given that  $\Lambda \cdot \eta$  is fairly independent of  $w_{\rm H_2O}$ , it is not surprising that the reported [30] value for  $[C_4 mim][Tf_2N]$  at 293 Κ.  $\Lambda \cdot \eta = 5.952 \cdot 10^{-6} \text{ S} \cdot \text{kg} \cdot \text{m} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$ , is within the range of our mixture values.

Earlier work [21,22] reporting  $\eta$  as a function of  $w_{\rm H_2O}$  showed that the relative decrease in  $\eta$  with increasing

 $w_{\rm H_{2O}}$  was greater for more viscous RTILs. That is, relatively larger changes in  $\eta$  were observed for more viscous RTILs for a given value of  $w_{\rm H_{2O}}$ . Given that, and the adherence to the Walden Rule exhibited by ([C<sub>4</sub>mim][Tf<sub>2</sub>N] + water), we predict that larger relative changes in  $\kappa$  will be observed for more viscous RTILs for a given  $w_{\rm H_{2O}}$  and smaller relative changes in  $\kappa$  will be observed for a given  $w_{\rm H_{2O}}$ .

An important conclusion from this work is that accurate measurement of  $\kappa$  requires careful control of the water content of the RTIL. Because of the magnitude of the effect of  $w_{\rm H_2O}$  on  $\kappa$ , conductivity data are suspect unless  $w_{\rm H_2O}$  is determined before *and after* the measurement of  $\kappa$ . Checking  $w_{\rm H_2O}$  after measuring  $\kappa$  is important because it is the only way to verify that  $w_{\rm H_2O}$  has not changed significantly during the measurement. To our knowledge, this is the first time such a precaution has been reported when measuring  $\kappa$  for an RTIL. We recommend that this precaution be generally adopted.

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#### References

- [1] T. Welton, Chem. Rev. 99 (1999) 2071-2083.
- [2] P.C. Trulove, R.A. Mantz, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003, pp. 103– 126.
- [3] J.S. Wilkes, ACS Sympos. Ser. 818 (2002) 214-229.
- [4] J. DuPont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667–3692.
- [5] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, Fluid Phase Equilib. 219 (2004) 93–98.
- [6] B.D. Fitchett, T.N. Knepp, J.C. Conboy, J. Electrochem. Soc. 151 (2004) E219–E225.
- [7] B. Garcia, S. Lavallée, G. Perron, C. Michot, M. Armand, Electrochim. Acta 49 (2004) 4583–4588.

- [8] H.A. Every, A.G. Bishop, D.R. MacFarlane, G. Orädd, M. Forsyth, Phys. Chem. Chem. Phys. 6 (2004) 1758–1765.
- [9] J.N. Barisci, G.G. Wallace, D.R. MacFarlane, R.H. Baughman, Electrochem. Commun. 6 (2004) 22–27.
- [10] A. Noda, K. Hayamizu, M. Watanabe, J. Phys. Chem. B 105 (2001) 4603–4610.
- [11] H. Every, A.G. Bishop, M. Forsyth, D.R. MacFarlane, Electrochim. Acta 45 (2000) 1279–1284.
- [12] H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, Y. Miyazaki, Chem. Lett. (2000) 922–923.
- [13] A.B. McEwen, H.L. Ngo, K. LeCompte, J.L. Goldman, J. Electrochem. Soc. 146 (1999) 1687–1695.
- [14] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168–1178.
- [15] K.R. Seddon, A. Stark, M.-J. Torres, Pure Appl. Chem. 72 (2000) 2275–2287.
- [16] C.D. Tran, S.H. De Paoli Lacerda, D. Oliveira, Appl. Spectrosc. 57 (2003) 152–157.
- [17] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, Phys. Chem. Chem. Phys. 3 (2001) 5192–5200.
- [18] J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 105 (2001) 10942–10949.
- [19] H. Xu, D. Zhao, P. Xu, F. Liu, G. Gao, J. Chem. Eng. Data 50 (2005) 133–135.
- [20] J. Zhang, W. Wu, T. Jiang, H. Gao, Z. Liu, J. He, B. Han, J. Chem. Eng. Data 48 (2003) 1315–1317.

- [21] J.A. Widegren, A. Laesecke, J.W. Magee, Chem. Commun. (2005) 1610–1612.
- [22] S. Pandey, K.A. Fletcher, S.N. Baker, G.A. Baker, Analyst 129 (2004) 569–573.
- [23] W. Xu, E.I. Cooper, C.A. Angell, J. Phys. Chem. B 107 (2003) 6170–6178.
- [24] E. Juhász, K.N. Marsh, in: K.N. Marsh (Ed.), Recommended Reference Materials for the Realization of Physicochemical Properties, Blackwell Scientific Publications, Oxford, 1987, pp. 371–378.
- [25] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, second ed., Butterworths Scientific Publications, London, 1959 (Chapter 5).
- [26] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156–164.
- [27] C.F. Poole, B.R. Kersten, S.S.J. Ho, M.E. Coddens, K.G. Furton, J. Chromatogr. 352 (1986) 407–425.
- [28] H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, J. Phys. Chem. B 108 (2004) 16593–16600.
- [29] M. Krummen, P. Wasserscheid, J. Gmehling, J. Chem. Eng. Data 47 (2002) 1411–1417.
- [30] R.A. Mantz, P.C. Trulove, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003, pp. 56– 68.
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