

Density, Viscosity, Speed of Sound, and Electrolytic Conductivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Its Mixtures with Water[†]

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Thermophysical properties were measured at ambient pressure for a high-purity sample of the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C₆mim][Tf₂N], and its mixtures with water. Density was measured with two vibrating tube densimeters in the temperature range (258.15 to 373.15) K. Dynamic viscosity was determined with a rotational coaxial cylinder measuring system over the temperature range (258.15 to 373.15) K, and kinematic viscosity was measured at (293.15 and 298.15) K with an Ubbelohde capillary viscometer. Speed of sound was measured in a pulse-echo cell over the temperature range (283.15 to 343.15) K. Electrolytic (ionic) conductivity was determined by use of the AC impedance bridge technique over the temperature range (288.15 to 323.15) K. For all of these measurements, special care was taken to control the concentration of water in the sample. The viscosity and electrolytic conductivity of ([C₆mim][Tf₂N] + H₂O) depend strongly on the concentration of water. By Karl Fischer titration, the H₂O mass fraction in the saturated ([C₆mim][Tf₂N] + H₂O) mixture was found to be 0.0111 ± 0.0004 at 298.15 K and 0.0101 ± 0.0004 at 293.15 K.

Introduction

This work is a contribution to the project titled Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems (project number 2002-005-1-100), which is sponsored by the International Union of Pure and Applied Chemistry (IUPAC). One of three objectives of this project is to establish the thermophysical properties of an ionic liquid reference system with reliable stability and purity.¹ To meet this objective, an international round-robin study of the thermophysical properties of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C₆mim][Tf₂N], was organized. This ionic liquid was chosen for a variety of reasons. It has a relatively low viscosity, which facilitates handling, and it is relatively hydrophobic, which facilitates purification. It has a normal melting point well below room temperature.² It has excellent thermal stability.³ The ions comprising the ionic liquid are in common use. The 1-*n*-alkyl-3-methylimidazolium class of cations is the most widely studied among ionic liquids. The bis(trifluoromethylsulfonyl)imide anion, [(F₃CSO₂)₂N][−] (abbreviated herein as [Tf₂N][−]), has good hydrolytic and electrochemical stability⁴ and is relatively hydrophobic.

Inconsistent sample purity is a likely reason for much of the disagreement in the reported thermophysical property data for ionic liquids.^{5–9} Water is arguably the most important impurity to consider, for three reasons. First, atmospheric moisture is ubiquitous. Second, even “hydrophobic” ionic liquids, which are not miscible with water, rapidly absorb water from the atmosphere^{5,10–12} or from moist surfaces. Hence, unless an ionic liquid is carefully dried and handled, it will be contaminated with water. Third, several published reports show that the presence of water can dramatically affect property measure-

ments, especially for transport properties.^{8,9,13–17} The [C₆mim][Tf₂N] used for this study is of known high purity, and special precautions were taken to control the concentration of water in it. For example, as recommended previously,^{8,9} coulometric Karl Fischer titration was used to determine the water concentration both before and after all property measurements.

Herein we report density (ρ), kinematic (ν) and dynamic (η) viscosity, speed of sound (u), and electrolytic conductivity (κ) as functions of temperature for dry [C₆mim][Tf₂N]. Additionally, we report measurements of the same properties for ([C₆mim][Tf₂N] + H₂O), with water mass fractions ($w_{\text{H}_2\text{O}}$) up to about 0.01. We also report the saturated water content of [C₆mim][Tf₂N] near room temperature. Data for the mixtures with water are interesting in their own right and also facilitate comparisons of the data from the round-robin study.

Experimental Section

Materials. (Trade names are given only to specify the experimental procedure and materials adequately and do not imply endorsement by the National Institute of Standards and Technology. Similar products by other manufacturers may work as well or better.) The [C₆mim][Tf₂N] was synthesized by Dr. Mark Muldoon, in Professor Joan Brennecke's laboratories at the University of Notre Dame, by use of 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 round-bottom flask fitted with a condenser and N₂ 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 held 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 1-bromohexane. The residual ethyl acetate was removed under reduced pressure at 323 K. Then, the 1-hexyl-3-methylimidazolium bromide ($x =$

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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 $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ 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 $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ 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 $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ 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 ($w_{\text{Br}} < 10^{-5}$). To remove traces of color and other impurities, the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ 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.

The $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was dried thoroughly before being used for measurements. The $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was placed in a spherical glass vacuum flask with a PTFE-coated magnetic stir bar. The vacuum flask was then attached to a vacuum line consisting of a vacuum manifold, a liquid nitrogen trap, and a mechanical vacuum pump. The $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was dried at room temperature with stirring at an ultimate pressure of no greater than 0.1 Pa. After drying, the vacuum flask was sealed with a PTFE valve and transferred into a glovebox. The nitrogen atmosphere in the glovebox contained less than 5 ppm of water, as continuously monitored with an aluminum oxide moisture analyzer.

Coulometric Karl Fischer titration on the dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ indicated that $w_{\text{H}_2\text{O}} \leq 10^{-5}$. The purity of the dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was also checked by ^1H and ^{19}F nuclear magnetic resonance (NMR) spectrometry. To check whether contamination or decomposition had occurred, NMR spectra were also obtained after each set of measurements. Ignoring water, the purity of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was always greater than 99.5 % by both ^1H and ^{19}F NMR. A fractional melting experiment performed in a different laboratory on the dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ indicated a purity of 99.76 mol %.² Shiflett and Yokozeki¹⁸ have reported additional chemical analyses of an aliquot of this material, including ion chromatography and elemental analysis, whose findings are consistent with a purity of no less than 99.5 %.

Determination of the Saturated Water Content of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ at (293.15 and 298.15) K. First, 3.2 mL of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ and 0.22 mL of water were transferred into a glass vial containing a magnetic stir bar. Then the vial was sealed with a septum cap, and the two phases were stirred vigorously for 24 h at 310 K. The vial was then sealed inside a larger container and immersed in a liquid bath maintained at 298.15 K. After a day of equilibration and phase separation, the vial was removed from the bath, a 0.25 mL sample of the ionic liquid layer was removed with a needle and syringe via the septum, and the vial was returned to the bath. Analysis of the ionic liquid layer by Karl Fischer titration gave a water mass fraction of $w_{\text{H}_2\text{O}} = 0.0112 \pm 0.0004$. After an additional day at 298.15 K, the ionic liquid layer was sampled again, and Karl Fischer analysis indicated that $w_{\text{H}_2\text{O}} = 0.0112 \pm 0.0004$. After a third day it was found that $w_{\text{H}_2\text{O}} = 0.0111 \pm 0.0004$. Then the bath temperature was lowered to 293.15 K to allow the mixture to

equilibrate and phases to separate for a day. At this point, Karl Fischer analysis of a sample of the ionic liquid layer showed $w_{\text{H}_2\text{O}} = 0.0101 \pm 0.0004$. After a second and third day at 293.15 K, $w_{\text{H}_2\text{O}}$ was also found to be 0.0101 ± 0.0004 . After an additional 2 months of equilibration time, Karl Fischer analysis showed no observable change in the water content of the ionic liquid layer.

Coulometric Karl Fischer Titration. At various times, the water concentration in the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was determined by use of a Metrohm 756 Karl Fischer coulometer. This instrument has a nominal detection limit of 10 μg of H_2O . The water concentration was determined before and after each set of property measurements. Unless otherwise stated, the value of $w_{\text{H}_2\text{O}}$ before and after a set of measurements differed by less than the experimental uncertainty in the Karl Fischer determination, and only the average value of $w_{\text{H}_2\text{O}}$ is given. The one exception was for the measurement of speed of sound and density by use of the pulse-echo instrument (see below); for such measurements, the values of $w_{\text{H}_2\text{O, before}}$ and $w_{\text{H}_2\text{O, after}}$ often differed significantly, so both are given. The procedure used for Karl Fischer titrations was based on ASTM test method E 1064 – 00, with three important modifications. First, the sample volume was typically 1.0 mL for the driest samples, instead of the 5 mL sample volume that the ASTM method recommends. Second, the syringe was not washed with (1 to 2) mL of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ before drawing a sample for titration. Third, all-plastic syringes were used instead of glass syringes.

Commercial liquid water standards, with nominal water mass fractions of $w_{\text{H}_2\text{O}} = 10^{-2}$, $w_{\text{H}_2\text{O}} = 10^{-3}$, and $w_{\text{H}_2\text{O}} = 10^{-4}$, were used to estimate the uncertainty of our method of water analysis. (These liquid water standards are packaged in glass ampoules and are a mixture of an organic liquid and water.) To illustrate, the following test was performed three times on three different days by use of a liquid water standard with $w_{\text{H}_2\text{O}} = (9.54 \pm 1) \cdot 10^{-5}$. A new ampoule of the standard was broken open, and immediately, 1 mL of the liquid was drawn into a weighed, 1 mL, all-plastic syringe via an oven-dried stainless steel needle. The needle was wiped clean with a tissue and pushed into a rubber block. The loaded syringe was reweighed before injecting the sample into the Karl Fischer coulometer. The raw data from the three titrations gave $w_{\text{H}_2\text{O}} = 10.39 \cdot 10^{-5}$, $9.58 \cdot 10^{-5}$, and $9.65 \cdot 10^{-5}$, and thus all three values are within the uncertainty limits given by the manufacturer of the water standard but do show expected scatter. Similar experiments were performed with the other liquid water standards. Not surprisingly, the uncertainty in $w_{\text{H}_2\text{O}}$ changes significantly as a function of the composition. At $w_{\text{H}_2\text{O}} = 10^{-2}$, the expanded uncertainty ($k = 2$) is estimated to be 4 % (i.e., $U = 0.04 w_{\text{H}_2\text{O}}$); at $w_{\text{H}_2\text{O}} = 10^{-3}$, the expanded uncertainty is estimated to be 6 %; and at $w_{\text{H}_2\text{O}} = 10^{-4}$, the expanded uncertainty is estimated to be 20 %.

Kinematic Viscosity Measurements with an Ubbelohde Capillary Viscometer at (293.15 and 298.15) K. The kinematic viscosity (ν) of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was measured at ambient pressure (approximately 83 kPa) with a commercially obtained Ubbelohde capillary viscometer (Schott-Geräte GmbH, size II). During calibration and measurement, the viscometer was immersed in an insulated, continuously stirred bath (ethylene glycol + water) whose temperature was regulated with a refrigerated circulator, an electric heater, and a precision temperature controller. The bath temperature was measured with an ITS-90 calibrated platinum resistance thermometer with an uncertainty of 0.01 K. Flow times were measured automatically with a Schott AVS/S measuring stand and an AVS 310 control unit. Each reported kinematic viscosity was determined by

averaging at least four successive flow times. The capillary viscometer was calibrated at NIST at 298.15 K by use of two different batches of S20 certified reference fluid from Cannon Instrument Company. The average value of the calibration constant, $0.08667 \text{ mm}^2 \cdot \text{s}^{-2}$, was used to calculate ν .

The capillary viscometer must be open to the atmosphere to function properly, but atmospheric moisture was effectively excluded in the following manner. The glass viscometer was dried overnight at 373 K and then transferred into a nitrogen atmosphere glovebox while still hot. In the glovebox, the viscometer was filled with the dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$. Then, loosely packed desiccant tubes filled with anhydrous calcium sulfate were attached to the open ends of the viscometer (a control experiment with the S20 reference fluid showed that the drying tubes did not affect the flow time). The viscometer was then removed from the glovebox, and a sample of the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was withdrawn from the viscometer via a septum and immediately analyzed by coulometric Karl Fischer titration. The viscometer was placed in the liquid bath, and following thermal equilibration, flow times were measured. Then the viscometer was removed from the bath, and another sample of the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was removed via the septum and immediately analyzed by coulometric Karl Fischer titration. Data for $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$ were collected in the same manner as for the dry $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$.

The uncertainty in the calibration constant for the viscometer translates to a relative standard uncertainty of 0.5 % in the viscosity measurement. Including fluctuations and temperature gradients, the uncertainty in the temperature is estimated to be 0.02 K, which leads to a relative standard uncertainty of 0.1 % in the viscosity measurement. For dry $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, the uncertainty in the water content leads to a relative standard uncertainty of 0.1 % in the viscosity measurement. The uncertainty in the flow time measurement is estimated to be 0.1 s, which leads to a relative standard uncertainty of less than 0.03 % in the viscosity measurement and therefore can be neglected. The Hagenbach (kinetic energy) correction may also be neglected since flow times were greater than 400 s. No correction was made to account for the difference in surface tension between the hydrocarbon-based calibration liquids and the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$. Hence, using standard techniques for the propagation of uncertainty, the expanded uncertainty ($k = 2$) in the measurement of ν by this method is 1 % (i.e., $U = 0.01 \nu$).

Viscosity and Density Measurements with the Stabinger Viscometer. The viscosity and density of dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ were measured simultaneously in a Stabinger viscometer (Anton Paar, model SVM3000). The Stabinger viscometer has two measuring cells—a vibrating U-tube for measuring density and a rotating concentric cylinders device for measuring viscosity. Both cells are housed in the same copper block, which has a thermoelectric temperature control system. The cells were filled with sample by connecting a loaded syringe to an inlet Luer port on the instrument. The liquid sample was then pushed into the instrument from the syringe, filling both of the cells. Any excess sample exits the instrument via an outlet Luer port on the instrument.

Measurements with the Stabinger viscometer were performed in the manner described in ASTM test method D 7042 – 04 but with special precautions to exclude atmospheric moisture. Before beginning a measurement, the two measuring cells were dried for at least an hour by flowing N_2 through the instrument via the inlet Luer port. In the meantime, an all-plastic syringe was loaded with $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ in the glovebox. The syringe

needle was pushed into a rubber block before removing the syringe from the glovebox. The N_2 line was removed from the inlet port and immediately replaced with the loaded syringe. The instrument was filled with about 3 mL of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ from the syringe. Then the outlet port was immediately capped with an empty, 1 mL, plastic syringe of known mass. With both ends of the instrument thus capped with syringes, density and viscosity were measured as a function of temperature. After measuring over the desired temperature range, an additional 1.0 mL of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was pushed into the instrument from the syringe on the inlet port. As a consequence, 1.0 mL of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was also pushed into the 1 mL syringe capping the outlet. The outlet syringe was removed and immediately replaced with an empty syringe. Then the 1.0 mL of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ in the outlet syringe was analyzed by Karl Fischer titration while another set of density and viscosity data was being collected in the Stabinger viscometer. After the second set of data was collected, another 1.0 mL of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was pushed into the instrument from the syringe on the inlet, and 1.0 mL of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was collected in the syringe capping the outlet. The outlet syringe was again replaced with an empty syringe, and the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ in the outlet syringe was analyzed by Karl Fischer titration. This process was repeated a total of four times. Four sets of data were collected.

ASTM test method D 7042 – 04 requires that the deviation between consecutive viscosity η determinations be within certain limits. Specifically, the stipulated repeatability for η at $T = 313.15 \text{ K}$ is $0.00101X$, where X is the average of the viscosities being compared (i.e., the two results should be repeatable to within 0.101 %). The stipulated repeatability at $T = 373.15 \text{ K}$ is $0.0003516 \cdot (X + 5)$. No repeatability criteria are given for η at other values of T . Once the repeatability criteria are met, the previously determined values are discarded and the last set of values is reported as the result. For the first experiment, in which η was measured from (293.15 to 373.15) K, deviations between the third and fourth data sets satisfy the repeatability criteria, but earlier pairs of data sets do not satisfy the criteria. Hence, only the fourth set of data from this experiment is reported here. The second experiment was done at lower temperatures, from (258.15 to 298.15) K, for which no repeatability criteria are given in the ASTM test method. For the sake of consistency, only the fourth data set from the second experiment is reported here. However, the repeatability was seen to be much poorer at lower temperatures—approximately $\pm 1 \%$ of η at 273.15 K and $\pm 2 \%$ of η at 258.15 K, which could be explained by a combination of larger temperature gradients on the measuring cell below ambient temperature and a steeper slope of the viscosity–temperature curve at these temperatures.

ASTM test method D 7042 – 04 also requires that the deviation between consecutive determinations of ρ be within certain repeatability limits. Specifically, the stipulated repeatability at $T = 288.15 \text{ K}$ is $\pm 0.46 \text{ kg} \cdot \text{m}^{-3}$, at $T = 313.15 \text{ K}$ is $\pm 0.30 \text{ kg} \cdot \text{m}^{-3}$, and at $T = 373.15 \text{ K}$ is $\pm 0.33 \text{ kg} \cdot \text{m}^{-3}$. No repeatability criteria are given for ρ at other values of T . Once the repeatability criteria are met, the previously determined values are discarded and the last set of values is reported as the result. For the first experiment, in which ρ was measured from (293.15 to 373.15) K, deviations between the third and fourth data sets satisfy the repeatability criteria, but earlier pairs of data sets do not satisfy the criteria. Hence, the fourth set of data from this experiment is reported here. For the second experiment, in which ρ was measured from (258.15 to 298.15) K, deviations between all the data sets satisfied the repeatability criteria. For the sake of consistency, the values from the fourth

data set are reported. In contrast to η , the deviations between consecutive ρ determinations with the Stabinger viscometer did not become larger at low temperatures; the repeatability of ρ was less than or equal to $\pm 0.3 \text{ kg}\cdot\text{m}^{-3}$ over the entire temperature range. The density data from the Stabinger viscometer were corrected for the viscosity effect on density determinations with vibrating tubes according to eq 1¹⁹

$$\Delta\rho = \rho[-0.5 + 0.45(\eta/\text{mPa}\cdot\text{s})^{1/2}]\cdot 10^{-4} \quad (1)$$

The largest correction was $1.9 \text{ kg}\cdot\text{m}^{-3}$ at 258.15 K (only the corrected densities are reported).

The accuracy of the Stabinger viscometer was checked with the certified reference fluids S20 and S200, which were obtained from Cannon Instrument Company. For these reference fluids, density values are given in the temperature range (293.15 to 373.15) K with an estimated uncertainty of $\pm 0.1 \text{ kg}\cdot\text{m}^{-3}$. The measured densities (corrected for the viscous effect, eq 1) differed from the reference values by as much as $\pm 0.7 \text{ kg}\cdot\text{m}^{-3}$ over that temperature range. The uncertainty in T is estimated to be less than or equal to 0.05 K, which leads to an uncertainty of $0.05 \text{ kg}\cdot\text{m}^{-3}$ in ρ for $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$. At 298.15 K, the estimated uncertainty in $w_{\text{H}_2\text{O}}$ is $2\cdot 10^{-5}$, which leads to an uncertainty of $0.03 \text{ kg}\cdot\text{m}^{-3}$ in ρ for $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$. Hence, the expanded uncertainty ($k = 2$) in the measurement of ρ from (293.15 and 373.15) K by this method is estimated to be $U = 2 \text{ kg}\cdot\text{m}^{-3}$. At lower temperatures, the uncertainty may be significantly larger.

For the S20 and S200 reference fluids, reference viscosity values are given in the temperature range (293.15 to 373.15) K with a relative standard uncertainty of no greater than 0.16 %. The measured viscosities differed from the reference values by as much as 0.9 % over that temperature range. The uncertainty in the temperature measurement is estimated to be no greater than 0.05 K, which leads to relative uncertainties in the viscosity of 0.4 % at 258.15 K, 0.2 % at 298.15 K, and 0.1 % at 373.15 K. At 298.15 K, the uncertainty in water content leads to a relative uncertainty of 0.1 % in the viscosity measurement. Hence, in the temperature range (293.15 to 373.15) K, the expanded uncertainty ($k = 2$) in the measurement of η by this method is estimated to be 2 % (i.e., $U = 0.02\eta$). The uncertainty is more difficult to estimate at lower temperatures, but the large deviations between consecutive η determinations (see above) indicate that the expanded uncertainty is at least 5 % (i.e., $U = 0.05\eta$) at the lowest temperatures.

Speed of Sound and Density Measurements as Functions of Temperature and Water Content. For dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, u and ρ were measured simultaneously in a commercial sound analyzer (Anton Paar model DSA5000) as a function of T from (283.15 to 343.15) K. Additionally, for $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$, u and ρ were measured simultaneously at $T = 298.15 \text{ K}$. This instrument has two measuring cells—a vibrating U-tube for measuring ρ and a pulse-echo cell for measuring u . Both cells are housed in the same metal block with a thermoelectric temperature control system. Both cells were calibrated with air and ultrapure water. Because of the similarity in the plumbing, measurements with the DSA5000 were performed in a manner analogous to the procedure described for the Stabinger viscometer. However, it was more difficult to keep the ionic liquid dry in the DSA5000; consequently, the uncertainty in water concentration is higher for measurements in this instrument than for the other instrument. To avoid bubble formation, the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was degassed under vacuum (with stirring) immediately prior to use. The DSA5000 automatically corrects for the effects of viscosity on density for samples with a

viscosity of less than $700 \text{ mPa}\cdot\text{s}$. The validity of this correction has been checked with Cannon viscosity standard liquids.^{20,21}

Fitzgerald's analysis²² of the accuracy of the density cell in the DSA5000 suggests that uncertainty for liquids between (650 and 1650) $\text{kg}\cdot\text{m}^{-3}$ and (0 to 600) $\text{mPa}\cdot\text{s}$ can be as small as $\pm 0.03 \text{ kg}\cdot\text{m}^{-3}$. The performance of the density cell was periodically checked by measuring ρ for degassed (boiled), deionized water (with a resistivity of $18 \text{ M}\Omega\cdot\text{cm}$) over the entire temperature range of (283.15 to 343.15) K. The difference between the measured density and the reference values never exceeded $\pm 0.04 \text{ kg}\cdot\text{m}^{-3}$ over the entire temperature range. The uncertainty in T is estimated²² to be 0.014 K, which translates into an uncertainty of $0.013 \text{ kg}\cdot\text{m}^{-3}$ in the measurement of ρ for $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$. However, we must factor into the analysis the observation that the ionic liquid became contaminated with water while in this instrument. In fact, $w_{\text{H}_2\text{O,after}} - w_{\text{H}_2\text{O,before}}$ was as high as $8.6\cdot 10^{-4}$, which causes the expanded uncertainty ($k = 2$) in the density measurement to be $U = 1.4 \text{ kg}\cdot\text{m}^{-3}$.

The performance of the sound analyzer was also periodically checked by measuring u for degassed (boiled), deionized water (with a resistivity of $18 \text{ M}\Omega\cdot\text{cm}$) over the entire temperature range of (283.15 to 343.15) K. The difference between the measured speed of sound and the reference values never exceeded $\pm 0.5 \text{ m}\cdot\text{s}^{-1}$ over the entire temperature range. The uncertainty in T is estimated²² to be 0.014 K, which translates into a negligible uncertainty of $0.03 \text{ m}\cdot\text{s}^{-1}$ in the measurement of u . The uncertainty in $w_{\text{H}_2\text{O}}$ was as high as $8.6\cdot 10^{-4}$, which leads to an uncertainty of $0.7 \text{ m}\cdot\text{s}^{-1}$ in the measurement of u . Hence, in the temperature range (283.15 to 343.15) K, the expanded uncertainty ($k = 2$) in the measurement of u by this method is estimated to be $U = 1.7 \text{ m}\cdot\text{s}^{-1}$.

Electrolytic Conductivity as a Function of Temperature and Water Content. A detailed description of the methodology used for these measurements can be found elsewhere,⁹ so only a brief description is provided here. The AC impedance bridge technique^{23,24} was used to measure κ as a function of T at about 0.1 MPa. Measurements were made with a small-volume commercial conductivity cell made of borosilicate glass with platinum black electrodes and a cell constant, K_{cell} , of 101.0 m^{-1} . The conductivity cell was connected to a commercial LCR (inductance, capacitance, and resistance) meter, which was programmed to scan a fixed set of frequencies from (0.8 to 5) kHz and return values of the capacitance and resistance at each frequency. The cell was calibrated at $T = 298.15 \text{ K}$ with commercially available conductivity standards (aqueous potassium chloride solutions) with $\kappa = (0.1 \pm 0.0005) \text{ S}\cdot\text{m}^{-1}$ and $\kappa = (1.0 \pm 0.0025) \text{ S}\cdot\text{m}^{-1}$. A test of the variation of the cell constant with temperature from (288.15 to 323.15) K showed a maximum variation of only 0.3 % from that at 298.15 K, an amount that was factored into the uncertainty of K_{cell} . Since the uncertainty of the calibration solutions (0.5 % for $0.1 \text{ S}\cdot\text{m}^{-1}$ and 0.25 % for $1.0 \text{ S}\cdot\text{m}^{-1}$) is comparable to the maximum temperature effect, we could justify the use of K_{cell} measured at 298.15 K for this work. 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) plugs. The cell was filled with dry $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ or with a mixture of $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$ in a glovebox. An aliquot of the sample was removed from the cell for Karl Fischer analysis. Then the cell was capped, brought out of the glovebox, and immersed in a constant-temperature bath filled with mineral oil. After each set of conductivity measurements, a second aliquot of the sample was removed and analyzed by Karl Fischer titration.

Table 1. Viscosity and Density of Dried ($w_{\text{H}_2\text{O}} = 10^{-5}$) $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, Determined with the Stabinger Viscometer

run no.	T/K	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$\nu^a/\text{mm}^2\cdot\text{s}^{-1}$
1	373.15	1304.8	7.463	5.719
1	363.15	1313.6	9.128	6.949
1	353.15	1322.5	11.38	8.607
1	343.15	1331.3	14.58	10.95
1	333.15	1340.3	19.22	14.34
1	323.15	1349.3	26.25	19.46
1	313.15	1358.3	37.41	27.54
1	303.15	1367.3	56.11	41.04
1	298.15	1371.9	70.29	51.24
1	293.15	1376.4	89.54	65.05
2	298.15	1371.6	70.09	51.10
2	293.15	1376.0	89.26	64.87
2	288.15	1380.5	115.8	83.91
2	283.15	1385.0	153.3	110.7
2	278.15	1389.5	207.6	149.4
2	273.15	1394.0	291.2	208.9
2	268.15	1398.5	417.4	298.5
2	263.15	1403.1	612.7	436.7
2	258.15	1407.6	941.8	669.1

^a Calculated, $\nu = \eta/\rho$.

The estimated uncertainty in the bath temperature (0.1 K) results in a relative standard uncertainty of 0.8 % in the measurement of κ . The uncertainty in K_{cell} results in a relative standard uncertainty of 0.7 % in the measurement of κ . The uncertainty in $w_{\text{H}_2\text{O}}$ for the dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ results in a relative standard uncertainty of 0.08 % in the measurement of κ . The uncertainty in the measurement of R with the precision LCR meter results in a relative standard uncertainty of 0.05 % in the measurement of κ . Hence, using standard techniques for the propagation of uncertainty, the expanded uncertainty ($k = 2$) in the measurement of κ is 2 % (i.e., $U = 0.02 \kappa$).

Results and Discussion

Saturated Water Content of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ Near Room Temperature. The saturated water content of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ was determined at (293.15 and 298.15) K by Karl Fischer titration. At 298.15 K, the water mass fraction in the saturated ionic liquid was $w_{\text{H}_2\text{O}} = 0.0111 \pm 0.0004$, and at 293.15 K, it was $w_{\text{H}_2\text{O}} = 0.0101 \pm 0.0004$. These values are in general agreement with two literature reports in which the saturated water content of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ at room temperature (i.e., without temperature control) was given as $w_{\text{H}_2\text{O}} = 0.011$ or $w_{\text{H}_2\text{O}} = 0.012$.^{25,26} For the property measurements on $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{water})$ that are described below, the water mass fraction was kept at $w_{\text{H}_2\text{O}} < 0.01$ to ensure a single phase.

Densities of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ and $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$ as Functions of Temperature. Two vibrating tube densimeters were used to measure ρ at ambient pressure. The vibrating tube densimeter in the Stabinger viscometer was used to collect data from (258.15 to 373.15) K for the dried ($w_{\text{H}_2\text{O}} = 10^{-5}$) ionic liquid (Table 1). For practical reasons, data for the entire temperature range were not collected in a single experiment. Instead, data were collected over the temperature range (293.15 to 373.15) K in one experiment and over the temperature range (258.15 to 298.15) K in a second experiment, with separate charges of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ used for each experiment. The overlapping data points from the two experiments, at (293.15 and 298.15) K, differ by no more than $0.4 \text{ kg}\cdot\text{m}^{-3}$. The data points at (258.15, 263.15, and 268.15) K are for the supercooled liquid.² Even at the lowest temperature, we never observed evidence of freezing in this instrument.

The vibrating tube densimeter in the DSA5000, which has a smaller temperature range and a smaller uncertainty than the

Table 2. Density and Speed of Sound of Dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, Determined with the DSA5000

run no.	T/K	$\rho/\text{kg}\cdot\text{m}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	$w_{\text{H}_2\text{O, before}}$	$w_{\text{H}_2\text{O, after}}$
1	343.15	1331.3	1128.4	$1\cdot 10^{-5}$	$8.7\cdot 10^{-4}$
1	333.15	1340.3	1149.8	$1\cdot 10^{-5}$	$8.7\cdot 10^{-4}$
1	323.15	1349.4	1171.5	$1\cdot 10^{-5}$	$8.7\cdot 10^{-4}$
1	313.15	1358.4	1193.3	$1\cdot 10^{-5}$	$8.7\cdot 10^{-4}$
1	303.15	1367.5	1215.5	$1\cdot 10^{-5}$	$8.7\cdot 10^{-4}$
1	298.15	1372.1	1226.8	$1\cdot 10^{-5}$	$8.7\cdot 10^{-4}$
1	293.15	1376.7	1238.4	$1\cdot 10^{-5}$	$8.7\cdot 10^{-4}$
1	283.15	1385.9	1262.0	$1\cdot 10^{-5}$	$8.7\cdot 10^{-4}$
2	343.15	1331.4	1129.6	$1\cdot 10^{-5}$	$5.1\cdot 10^{-4}$
2	333.15	1340.4	1150.4	$1\cdot 10^{-5}$	$5.1\cdot 10^{-4}$
2	323.15	1349.4	1171.6	$1\cdot 10^{-5}$	$5.1\cdot 10^{-4}$
2	313.15	1358.4	1193.4	$1\cdot 10^{-5}$	$5.1\cdot 10^{-4}$
2	303.15	1367.6	1215.6	$1\cdot 10^{-5}$	$5.1\cdot 10^{-4}$
2	298.15	1372.2	1226.9	$1\cdot 10^{-5}$	$5.1\cdot 10^{-4}$
2	293.15	1376.8	1238.5	$1\cdot 10^{-5}$	$5.1\cdot 10^{-4}$
2	283.15	1386.0	1262.4	$1\cdot 10^{-5}$	$5.1\cdot 10^{-4}$

Table 3. Density and Speed of Sound of $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$, Determined with the DSA5000

T/K	$\rho/\text{kg}\cdot\text{m}^{-3}$	$u/\text{m}\cdot\text{s}^{-1}$	$w_{\text{H}_2\text{O, before}}$	$w_{\text{H}_2\text{O, after}}$
298.15	1372.07	1226.6	$3\cdot 10^{-5}$	$4\cdot 10^{-5}$
298.15	1370.45	1227.4	$1.02\cdot 10^{-3}$	$1.10\cdot 10^{-3}$
298.15	1367.04	1230.3	$7.22\cdot 10^{-3}$	$7.41\cdot 10^{-3}$

densimeter in the Stabinger viscometer, was used to collect data from (283.15 to 343.15) K. Table 2 shows data from two experiments that were performed months apart with separate charges of the ionic liquid. The repeatability of ρ for the two experiments in the DSA5000 is less than or equal to $0.1 \text{ kg}\cdot\text{m}^{-3}$ over the entire temperature range. The difference between ρ from the DSA5000 and ρ from the Stabinger viscometer was no greater than $1.0 \text{ kg}\cdot\text{m}^{-3}$ over the entire temperature range, which is smaller than the estimated uncertainty of either measurement. Unfortunately, for these measurements the higher accuracy of the DSA5000 was largely negated by the uncertainty in $w_{\text{H}_2\text{O}}$. As shown in Table 2, $w_{\text{H}_2\text{O, after}} - w_{\text{H}_2\text{O, before}} = 8.6\cdot 10^{-4}$ for the first experiment and $5.0\cdot 10^{-4}$ for the second experiment. This can be explained by the instrument's design, calibration checks, and flushing procedures. The DSA5000 consists of a cylindrical cell for sound speed (with a large surface area and an inside diameter much larger than that of the inside diameter of the flow tubing) which then feeds the vibrating tube densimeter. Following the manufacturer's recommended procedures, prior to measurements on an unknown, the instrument's calibration was checked with water, and then the instrument was flushed. It is reasonable to speculate that flushes did not fully dry the instrument, and thus the hygroscopic ionic liquid was contaminated by trace amounts of water. Most of the trace water was probably adsorbed on the walls of the sound speed cell, whose large diameter relative to that of the flow tubing would make it not as conducive to flushing as the densimeter tubing. For future studies of hygroscopic fluids, we recommend adding to the manufacturer's procedure a final hot dry nitrogen flush for 30 min at 60 °C to remove any remaining adsorbed water. Because of the change in $w_{\text{H}_2\text{O}}$ over the course of each experiment, the densities in Table 2 have approximately the same uncertainty as the densities in Table 1. This is an excellent example of why it is important to determine $w_{\text{H}_2\text{O}}$ after property measurements on ionic liquids. Even for this relatively hydrophobic ionic liquid, changes in $w_{\text{H}_2\text{O}}$ during the measurement were the largest source of uncertainty.

The effect of $w_{\text{H}_2\text{O}}$ on ρ was determined at 298.15 K by preparing mixtures of $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$ with $w_{\text{H}_2\text{O}}$ up to about $7.3\cdot 10^{-3}$ (Table 3). The total decrease in ρ with added H_2O was about $5 \text{ kg}\cdot\text{m}^{-3}$ (i.e., 0.37 %), which is consistent

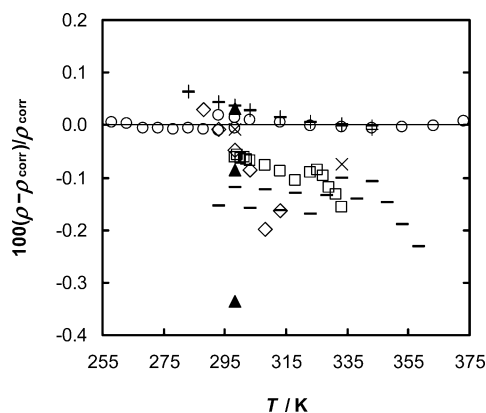


Figure 1. Deviation of ρ from a correlation (eq 2) of the density data collected with the Stabinger viscometer: \circ , Table 1; $+$, Table 2; \blacktriangle , Table 3; $-$, ref 28; \square , ref 29; \diamond , ref 31; \times , ref 32.

with analogous experiments for related ionic liquids.²⁷ For these experiments, the change in $w_{\text{H}_2\text{O}}$ over the course of each measurement was limited by minimizing the residence time of the ionic liquid in the instrument. For the density data shown in Table 2, uncertainties due to changes in $w_{\text{H}_2\text{O}}$ were determined by interpolation of the first two data points in Table 3.

The data for ρ as a function of T (at $p \approx 83$ kPa) that were measured with the Stabinger viscometer are correlated to within 0.02 % by the quadratic equation

$$\rho/(\text{kg}\cdot\text{m}^{-3}) = 4.533 \cdot 10^{-5}(T/\text{K})^2 - 0.92274(T/\text{K}) + 1642.73 \quad (2)$$

Figure 1 shows deviations from this correlation for all the density data reported herein, including ρ as a function of $w_{\text{H}_2\text{O}}$ at 298.15 K. Published density data ($p \approx 101$ kPa), from Kato and Gmehling,²⁸ Rebelo and co-workers,²⁹ Watanabe and co-workers,^{30,31} and Canongia Lopes and co-workers,³² are also shown on the deviation plot. Agreement between the data sets is good—almost all of the data points fall within ± 0.2 % of the data from the Stabinger viscometer (which has an estimated uncertainty of about 0.15 % over the relevant temperature range).

Viscosities of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ and $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$ as a Function of Temperature. Viscosities were determined at ambient pressure by two methods. First, an Ubbelohde capillary viscometer was used to determine the kinematic viscosities (ν) of dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ and $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$ at temperatures of (293.15 and 298.15) K. Second, a Stabinger viscometer was used to measure the dynamic viscosity (η) of dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ over the temperature range (258.15 and 373.15) K. By using the simple relationship between dynamic and kinematic viscosity, $\eta = \nu \cdot \rho$, results of the two methods can be compared.

Data obtained with the Ubbelohde capillary viscometer are shown in Table 4. On the basis of the reported behavior of $([\text{C}_2\text{-mim}][\text{Tf}_2\text{N}] + \text{water})$ and $([\text{C}_4\text{mim}][\text{Tf}_2\text{N}] + \text{water})$,^{8,15,27} ν was expected to vary strongly with $w_{\text{H}_2\text{O}}$. At this point in the discussion, it is convenient to introduce a dimensionless coefficient of dilution for a generalized property z , namely, $\Phi_z = (\partial z / \partial a) / \partial w_{\text{H}_2\text{O}}$. This quantity represents the fractional change in a property from a dry to a wet condition per mass fraction of solvent added to a dry substance. It can be calculated directly from experimental observations. At 298.15 K, we calculated an aqueous dilution coefficient for kinematic viscosity (in Table 4) of $\Phi_\nu = (\partial \nu / \partial a) / \partial w_{\text{H}_2\text{O}} = -47$, which implies that an addition of 1 % (mass) water decreases the kinematic viscosity by 47 %. Indeed, it is no surprise that at 298.15 K ν decreases by 29

Table 4. Kinematic Viscosities of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ and $([\text{C}_6\text{mim}][\text{Tf}_2\text{N}] + \text{H}_2\text{O})$ Determined with the Ubbelohde Capillary Viscometer

T/K	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$w_{\text{H}_2\text{O}}$
293.15	65.30	$2 \cdot 10^{-5}$
293.15	61.57	$1.1 \cdot 10^{-3}$
293.15	45.49	$8.2 \cdot 10^{-3}$
298.15 ^a	51.18 ^a	$1 \cdot 10^{-5}$
298.15	51.34	$2 \cdot 10^{-5}$
298.15	48.52	$1.12 \cdot 10^{-3}$
298.15	36.31	$8.19 \cdot 10^{-3}$

^a This measurement was done with a separate charge of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$.

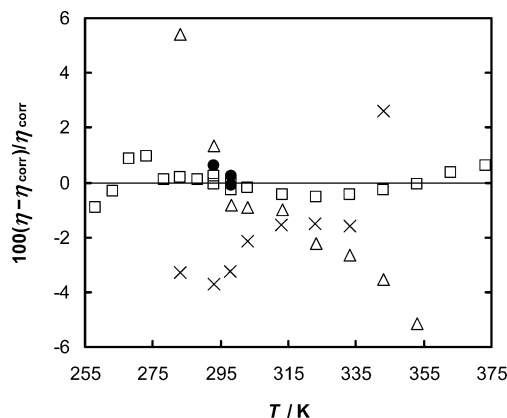


Figure 2. Deviation of η from a correlation (eq 3) of the viscosity data collected with the Stabinger viscometer: \square , Table 1; \bullet , Table 4 (after converting from ν to η); \times , ref 3; \triangle , ref 31.

% when $w_{\text{H}_2\text{O}}$ increased from $1 \cdot 10^{-5}$ (=dried) to $8.19 \cdot 10^{-3}$. The inverse of the dilution coefficient $\Phi_\nu^{-1} = 0.021$ gives us the increase in percentage mass fraction of $w_{\text{H}_2\text{O}}$ which is sufficient to cause a decrease of 1 % in ν . For the dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ at 298.15 K, ν was determined twice using separate charges of ionic liquid. These two determinations were performed a year apart and give an idea of the repeatability of the measurement. No correction was made to account for the difference in surface tension between the hydrocarbon-based calibration liquids and the $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$. However, the agreement between the capillary measurements and the other measurements shown in Figure 2 suggests that the effect of surface tension is relatively small.

For the dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, η was measured as a function of T (at $p \approx 83$ kPa) from (258.15 to 373.15) K with the Stabinger viscometer. These data, given in Table 1, are correlated to within 1 % by the VTF equation

$$\ln(\eta/\eta^\circ) = e + f/(g + T) \quad (3)$$

where $\eta^\circ = 1$ mPa·s. The parameters e , f , and g for the correlation are -2.13683 , 882.430 K, and -160.036 K, respectively. Figure 2 shows the deviations of the Stabinger viscosity data from the VTF correlation. The Ubbelohde viscosity data (after converting to dynamic viscosity) and two literature data sets^{3,30,31} are also shown in Figure 2. The overlapping data points (at (293.15 and 298.15) K) from the two experiments in the Stabinger viscometer agree to within 0.3 %. The viscosities from the Stabinger viscometer agree with the viscosities from the Ubbelohde capillary viscometer to within 0.7 %, which is smaller than the uncertainty of either measurement. The literature data sets agree with the correlation to better than 6 %.

Speed of Sound as a Function of Temperature and Water Content. For the dried $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, u was measured as a

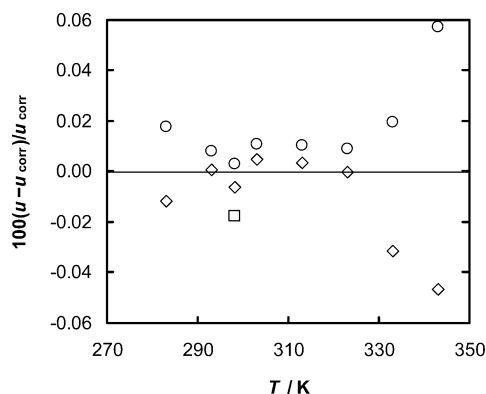


Figure 3. Deviation of u from a correlation (eq 4) of the data: \diamond , Table 2, $w_{\text{H}_2\text{O,after}} = 8.7 \cdot 10^{-4}$; \circ , Table 2, $w_{\text{H}_2\text{O,after}} = 5.1 \cdot 10^{-4}$; \square , Table 3, $w_{\text{H}_2\text{O,after}} = 4 \cdot 10^{-5}$.

Table 5. Electrolytic (Ionic) Conductivities of [C₆mim][Tf₂N] and ([C₆mim][Tf₂N] + H₂O)

T/K	$\kappa/\text{S}\cdot\text{m}^{-1}$	$w_{\text{H}_2\text{O}}$
288.15	0.135	$1 \cdot 10^{-5}$
293.15	0.173	$1 \cdot 10^{-5}$
298.15	0.218	$1 \cdot 10^{-5}$
308.15	0.328	$1 \cdot 10^{-5}$
323.15	0.548	$1 \cdot 10^{-5}$
288.15	0.142	$9.4 \cdot 10^{-4}$
293.15	0.180	$9.4 \cdot 10^{-4}$
298.15	0.227	$9.4 \cdot 10^{-4}$
308.15	0.340	$9.4 \cdot 10^{-4}$
323.15	0.566	$9.4 \cdot 10^{-4}$
293.15	0.232	$7.27 \cdot 10^{-3}$
298.15	0.289	$7.27 \cdot 10^{-3}$
293.15	0.237	$7.84 \cdot 10^{-3}$
298.15	0.295	$7.84 \cdot 10^{-3}$
293.15	0.246	$8.98 \cdot 10^{-3}$
298.15	0.306	$8.98 \cdot 10^{-3}$

function of T (at $p \cong 83$ kPa) from (283.15 to 343.15) K with the pulse-echo cell of the DSA5000 (Table 2). These data are correlated to within 0.06 % by the polynomial equation

$$u/(\text{m}\cdot\text{s}^{-1}) = -2.83114 \cdot 10^{-5}(T/\text{K})^3 + 2.91637 \cdot 10^{-2}(T/\text{K})^2 - 1.21307 \cdot 10^1(T/\text{K}) + 3.00149 \cdot 10^3 \quad (4)$$

Figure 3 shows deviations of the data from this correlation. Frez et al.³³ used the transient grating technique to determine that $u = (1232 \pm 11)$ m·s⁻¹ at 296.85 K. This data point is consistent with our measurements, although its low accuracy limits the value of the comparison. We are not aware of any other reports of u for [C₆mim][Tf₂N].

We also determined u for ([C₆mim][Tf₂N] + water), with $w_{\text{H}_2\text{O}}$ as high as $7.4 \cdot 10^{-3}$ (Table 3). At 298.15 K, u increased by 3.7 m·s⁻¹ (0.30 %) when $w_{\text{H}_2\text{O}}$ increased from $4 \cdot 10^{-5}$ to $7.4 \cdot 10^{-3}$. Similar to our treatment of kinematic viscosity, we can calculate dilution coefficients for speed of sound, $\Phi_u = (\delta u/u_d)/\delta w_{\text{H}_2\text{O}}$, and for density, $\Phi_\rho = (\delta \rho/\rho_d)/\delta w_{\text{H}_2\text{O}}$. At 298.15 K, coefficients $\Phi_u = 0.41$ and $\Phi_\rho = -0.50$ were calculated with the data in Table 3. It is clear from these coefficients that the relative change in u is nearly the same magnitude as the relative change in ρ , but with the opposite sign.

Electrolytic Conductivity as a Function of Temperature and Water Content. The electrolytic conductivity, κ , was determined by use of the AC impedance bridge technique (Table 5). As described in our earlier work⁹ with this technique and that of others,^{23,24} resistance R values were measured over a range of frequencies f . Those R values were fitted with two linear

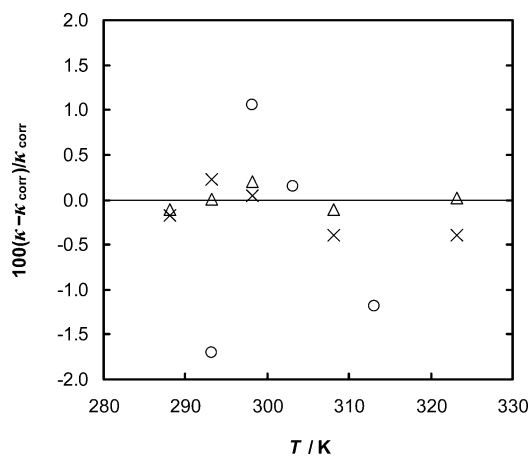


Figure 4. Deviation of κ from a correlation (eq 5) of the data: \triangle , Table 5; \times , ref 9; \circ , ref 31.

equations, one in terms of f^{-1} and the other in terms of $f^{-0.5}$. Then the best fitted equation (with r -squared > 0.99) was extrapolated to f_∞ , which gives a value of R_∞ whose inverse is the conductance G from which the electrolytic conductivity $\kappa = K_{\text{cell}} \cdot G$ can be calculated. In the majority of cases, R for a dry ionic liquid was more linear with f^{-1} , and R for aqueous mixtures was more linear with $f^{-0.5}$. Since the maximum change in R is 0.6 % when extrapolating from the highest measured frequency of 5 kHz to ∞ , the fitted equation is not a limiting factor.

For dried ($w_{\text{H}_2\text{O}} = 1 \cdot 10^{-5}$) ionic liquid, κ was determined at temperatures of (288.15, 293.15, 298.15, 308.15, and 323.15) K (at $p \cong 83$ kPa)—a repeat of measurements we reported previously⁹ using the same equipment and the same batch of [C₆mim][Tf₂N]. These values differ from the previously reported values by no more than 0.4 %, well within the uncertainty of the measurements. For dried [C₆mim][Tf₂N], the data for κ as a function of T can be correlated to within 0.2 % with the quadratic equation

$$\kappa/(\text{S}\cdot\text{m}^{-1}) = 1.421728 \cdot 10^{-4}(T/\text{K})^2 - 7.511157 \cdot 10^{-2}(T/\text{K}) + 9.973997 \quad (5)$$

Figure 4 shows deviations of the data from this correlation, along with deviations of our previously reported⁹ data. A literature data set (circles) from Watanabe and co-workers is also shown in Figure 4. These data all agree within the uncertainty of our measurements.

We also determined κ for ([C₆mim][Tf₂N] + water), with $w_{\text{H}_2\text{O}}$ as high as $8.98 \cdot 10^{-3}$ (Table 5). On the basis of the reported behavior of ([C₄mim][Tf₂N] + water),⁹ κ was expected to depend strongly on $w_{\text{H}_2\text{O}}$. Indeed, at 298.15 K, κ increased by 40 % when $w_{\text{H}_2\text{O}}$ increased from $1 \cdot 10^{-5}$ to $8.98 \cdot 10^{-3}$. At 298.15 K, an increase in $w_{\text{H}_2\text{O}}$ of only $2.2 \cdot 10^{-4}$ is sufficient to increase κ by 1 %. At this temperature, the calculated coefficient of dilution for electrolytic conductivity, $\Phi_\kappa = (\delta \kappa/\kappa_d)/\delta w_{\text{H}_2\text{O}} = 45$, is close in magnitude to that for kinematic viscosity, $\Phi_\nu = -47$, but with opposite sign. As shown by the calculated dilution coefficients Φ_ν , Φ_κ , Φ_ρ , and Φ_u , the relative changes in both κ and η with increasing $w_{\text{H}_2\text{O}}$ are nearly 2 orders of magnitude larger than the relative changes in either u or ρ . Last, coefficients of dilution should facilitate more meaningful comparisons, on a common composition basis, between different sets of experimental data when measurements on samples with different water concentrations are involved.

Acknowledgment

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