Measurement of the Viscosity, Density, and Electrical Conductivity of 1-Hexyl-3-methylimidazolium Bis(trifluorosulfonyl)imide at Temperatures between (288 and 433) K and Pressures below 50 MPa

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The viscosity, density, and electrical conductivity of 1-hexyl-3-methylimidazolium bis(trifluorosulfonyl)imide have been measured at temperatures from (288 to 433) K and at pressures up to 50 MPa. A vibrating wire viscometer was used for the measurements of viscosity that have an expanded uncertainty ($k = 2$) of ± 2 %. The density was obtained from a vibrating tube densimeter with an expanded uncertainty ($k = 2$) of ± 0.3 %. The electrical conductivity $\kappa(f \rightarrow \infty)$ was determined from impedance measurements at frequencies in the range (0.5 to 10) kHz with an expanded ($k = 2$) uncertainty of ± 2 %. All measurements were conducted with a sample distributed by NIST as part of an IUPAC project. The water mass fraction was determined before and after the measurements. The viscosity and density of a sample with initial water content of $7 \cdot 10^{-6}$ were represented by interpolating expressions with standard deviations of 0.4 % and 0.03 %, respectively. Differences between the experimental and calculated values are comparable with the expanded ($k = 2$) uncertainties. For temperatures that overlap the temperature range (288 to 433) K at $p = 0.1$ MPa, literature values of density differ by $\leq \pm 0.2$ % while the reported viscosities differ by $\leq \pm 7$ % from these empirical representations of the measurements. There are no values of the viscosity at $p > 0.1$ MPa reported in the literature to compare our results. At $p > 0.1$ MPa, the literature values for density reported by Gomes de Azevedo (*J. Chem. Thermodyn.* **2005**, *37*, 888−899) deviate from our smoothing equation by less than −0.2 % at temperatures and pressure that overlap ours. The electrical conductivity was determined on a sample with initial water mass fraction of $90 \cdot 10^{-6}$. The results were represented within the expanded uncertainty by an empirical function against which the literature values differed by no more than ± 5 %.

Introduction

For a room-temperature ionic liquid, the thermophysical properties reported in the archival literature often differ from various sources by many times the estimated expanded uncertainty associated with the measurement technique. A plausible explanation for these discrepancies is provided by the presence of impurities of which the most prevalent is water. Even so-called “hydrophobic ionic liquids”, which are immiscible with water, absorb atmospheric water vapor, and the presence of water has been shown to introduce a significant and systematic error in the measured physiochemical properties particularly for transport phenomena.[1,2] Consequently, under the auspices of the International Union of Pure and Applied Chemistry (IUPAC), a project entitled “Thermodynamics of Ionic Liquids, Ionic Liquid Mixtures, and the Development of Standardized Systems” (project number 2002-005-1-100)[3] has been established to provide reference values for the thermophysical properties of an ionic liquid with a 1-hexyl-3-methylimidazolium cation (herein after known by the acronym [hmim] and in other publications as $[C6mim]^+$) and a bis(trifluoromethylsulfonyl)-imide, $[(F_3CSO_2)_2N]^-$ (abbreviated herein after as $[Tf_2N]^-$), anion. The $[hmim][Tf_2N]$ was chosen because the 1-alkyl-3-methylimidazolium cation is the most widely studied among ionic liquids and, when compared to other ionic liquids, has a relatively low viscosity, hydrophobicity, and melting point, which is well below room temperature,[4] and is thermally stable.[5]

This article reports measurements of the viscosity, density, and electrical conductivity of $[hmim][Tf_2N]$ at temperatures in the range (288 to 433) K and pressures between (0.1 and 50) MPa. This work constitutes a contribution to the IUPAC project.

For $[hmim][TF_2N]$ at $p = 0.1$ MPa and temperatures from (258 to 373) K, there are four publications reporting the viscosity[5,1,6,7] and seven articles reporting the density at $p \approx 0.1$ MPa[1,6,8−12] for which refs 1, 7, and 12 were performed on an aliquot of the sample described in ref 3 and this work. References 11 and 12, both from the same laboratory, report densities at pressures up to 65 MPa, and those of ref 12 were obtained on an aliquot of the same sample as that used in this work. The results reported here have been compared with all these measurements. The electrical conductivity has been reported by Widegren and Magee,[1] Widegren et al.,[13] and Tokuda et al.,[10] and our results are also compared with these independent sources.

Experimental

The $[hmim][TF_2N]$ was obtained from a batch prepared by Notre Dame University and distributed through the National Institute of Standards and Technology in vacuum-sealed Schlenk

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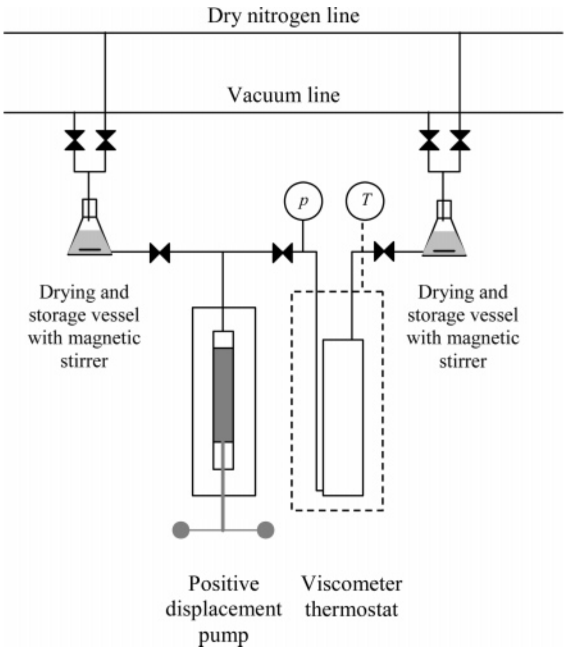

Figure 1. Schematic of the apparatus used to dry the 1-hexyl-3-methylimidazolium bis(trifluorosulfonyl)imide and transfer an aliquot to the vibrating wire viscometer.

tubes as part of an IUPAC project.[3] The procedures used to synthesize the [hmim][Tf_2N] have been described in, for example, ref 1. Excluding the impurity water, the [hmim][Tf_2N] had a mass fraction purity > 99.5 % as determined by both ^1H and ^{19}F NMR, while a fractional melting experiment performed on dry [hmim][Tf_2N] provided a mole fraction purity of 99.76 %.[1] The sample was stirred under a vacuum at room temperature, as shown in Figure 1, to remove water prior to use. The mass fraction of water in the sample was determined by Karl Fisher titration with a Radiometer Analytical Titrator, TIM 550, according to the procedure recommended by ASTM, before commencing measurements and also on an aliquot after cessation of data acquisition. The viscosity was determined for two samples: (A), where the mass fraction of water $w(H_2O)$ was $43 \cdot 10^{-6}$ before and $410 \cdot 10^{-6}$ after the measurements; and (B), for which $w(H_2O)$ was $7 \cdot 10^{-6}$ before and $117 \cdot 10^{-6}$ after the measurements. Sample A was used for the density measurements. The samples were degassed under a vacuum for at least 12 h prior to use. A third sample, with a $w(H_2O)$ of $90 \cdot 10^{-6}$ before and $180 \cdot 10^{-6}$ after the measurements, was used to obtain the electrical conductivity. The repeatability of the Karl Fisher titration was, with a standard of $w(H_2O) = 10^{-4}$, $\pm 10 \cdot 10^{-6}$ and is consistent with the expanded uncertainties of 20 % for $w(H_2O) = 10^{-4}$; at $w(H_2O) = 10^{-3}$, the expanded uncertainty decreases to be about 6 %.[13] The procedures used to clean and dry the apparatus have been described in detail elsewhere,[1,13] while an aliquot was transferred to the viscometer as illustrated in Figure 1.

The viscosity was measured with a vibrating wire viscometer that had previously been used to measure the viscosities between (0.3 and 100) mPa·s at temperatures from (298 to 423) K and pressures from (0.1 to 70) MPa for methylbenzene and two certified reference fluids for viscosity,[14] liquid cyclopentane,[15] and diisodecyl phthalate (DIDP).[16] The measurements reported in refs 14−16 cover the range of viscosity, temperature, and pressure encountered in this work. The apparatus, working equations, and analyses of the vibrating wire viscometer, with a wire diameter of about 0.15 mm, have been described in refs 14 and 17. The expanded ($k = 2$) uncertainty of the viscosity so obtained is, based on our previous work,[14,17−19] ± 2 %. The electrical conductivity of [hmim][Tf_2N], with $w(H_2O)$ between $(90 \text{ and } 180) \cdot 10^{-6}$, was found to be $< 0.5\ S \cdot m^{-1}$, and this conductivity introduces a negligible additional systematic error in the determination of viscosity from measurements of the width of the fundamental resonance frequency of the vibrating wire. The sinusoidal voltage applied to the wire was generated by a lock-in amplifier, and the amplitude varied between (1 and 2) mV.

Densities were measured with an Anton Paar vibrating tube densimeter (model DMA 512 P) for operation at pressures in the range (0.1 to 70) MPa. The instrument was calibrated as described in ref 16 and has an expanded uncertainty of ± 0.3 %. The correction to the density for viscous damping, discussed elsewhere,[18] at the viscosities reported here (< 110 mPa·s) was always < 0.05 %. The working equations for the vibrating wire viscometer require values of density with an uncertainty of ± 2 % to yield an uncertainty of ± 1 % in viscosity.

A conductivity cell, formed from borosilicate glass, with two platinum black electrodes (LKB model 5312 A flow cell) was used for the measurements. The resistance $R(f)$ of the cell was determined with an impedance (LCR, inductive-capacitive-resistance) meter (HP model 4261A) operated at 1 V rms in the series C and R mode at frequencies of (0.5, 1, 2, 4, 6, and 10) kHz. For the determination of κ, $R(f \rightarrow \infty)$ was obtained at each temperature from

$$R(f)/\Omega = \left(\frac{\mathrm{d}R}{\mathrm{d}f^{-1/2}}\right) \cdot f^{-1/2} + R(f \rightarrow \infty) \qquad (1)$$

which represented the measurements within $100 \cdot \sigma(R)/\langle R \rangle < \pm 0.45$; $100 \cdot \sigma(R)/\langle R \rangle$ increased from 0.01 at $T = 278$ K to 0.45 at $T = 323$ K. To determine, at each temperature, the variations of the measurements with respect to time and frequency, the frequency was first increased from (0.5 to 10) kHz and repeated at frequencies of (0.5 and 1) kHz. In all cases, the two set of results obtained at (0.5 and 1) kHz differed by <± 0.5 %. The values of $R(f \rightarrow \infty)$ were used to determine the conductance, $G = R^{-1}$, and combined with the cell constant K to determine the conductivity from[20]

$$\kappa = G \cdot K \qquad (2)$$

The cell constant $K \approx d/A$, where d is the distance between the electrodes and A is the area of the electrode, was determined by the manufacturer to be $\langle K(f \rightarrow \infty) \rangle = 90.1\ m^{-1}$.

The expanded uncertainty in $R(f)$ obtained with the LCR meter was $10^{-3} \cdot R$, and the expanded uncertainty in the conductivity was ± 2 %[13] determined by combining in quadrature the uncertainties arising from the calibration to obtain K and the procedure used to determine $R(f \rightarrow \infty)$.

Temperatures of the densimeter, viscometer, and conductivity cell were measured with uncertainties of (± 0.02, ± 0.01, and ± 0.01) K, respectively, on ITS 90. Pressures were generated with a hydraulic pump and measured, relative to atmospheric pressure, using dial gauges that were, when calibrated against a dead-weight gauge, found to have an uncertainty of ± 0.05 MPa. Ambient pressure was obtained from a mercury barometer with an uncertainty of ± 0.1 kPa.

Results and Discussion

The density of [hmim][Tf_2N] is given in Table 1. the viscosities for samples A and B with different water mass fraction are listed in Table 2, and the electrical conductivity is

Table 1. Densities ρ of [hmim][Tf$_2$N] Sample A with w(H$_2$O) between (43 and 410)·10^{-6} Obtained with the Vibrating Tube Densimeter at Temperature T and Pressure p

T/K	p/MPa	ρ/kg·m^{-3}	T/K	p/MPa	ρ/kg·m^{-3}
298.15	0.10	1371	348.15	40.0	1359
298.15	10.0	1379	373.15	0.10	1303
298.15	20.0	1386	373.15	10.0	1314
298.15	30.0	1393	373.15	20.0	1321
298.15	40.0	1399	373.15	30.0	1332
323.15	0.10	1349	373.15	40.0	1339
323.15	10.0	1357	398.15	10.0	1292
323.15	20.0	1364	398.15	20.0	1301
323.15	30.0	1372	398.15	30.0	1311
323.15	40.0	1378	398.15	40.0	1319
348.15	0.10	1325	423.15	10.0	1270
348.15	10.0	1334	423.15	20.0	1279
348.15	20.0	1343	423.15	30.0	1292
348.15	30.0	1352	423.15	40.0	1299

Table 2. Viscosities η of [hmim][Tf$_2$N] for Both Sample A, of Water Mass Fraction w(H$_2$O) between (43 and 410)·10^{-6}, and Sample B, of Water Mass Fraction w(H$_2$O) between (7 and 117)·10^{-6}, at Temperatures T and Pressure p

T	p	η(A)	η(B)	T	p	η(A)	η(B)
K	MPa	mPa·s	mPa·s	K	MPa	mPa·s	mPa·s
288.15	0.10	111		353.15	30.0	14.5	15.3
293.15	0.10	86	90	353.15	40.0	15.8	16.7
293.15	10.0	98	102	353.15	50.0		18.1
298.15	0.10	68		363.15	0.10		9.2
298.15	10.0	78		373.15	0.10	7.2	7.5
298.15	20.0	86		373.15	10.0	7.9	8.3
298.15	30.0	96		373.15	20.0	8.5	9.0
298.15	40.0	107		373.15	30.0	9.4	9.6
303.15	0.10		57	373.15	40.0	10.0	10.8
303.15	10.0		66	393.15	0.10	5.0	5.2
303.15	20.0		72	393.15	10.0	5.5	5.7
303.15	30.0		81	393.15	20.0	5.9	6.2
313.15	0.10	36.2	37.7	393.15	30.0	6.4	6.8
313.15	10.0	40.8	42.7	393.15	40.0	6.9	7.2
313.15	20.0	45.4	46.2	393.15	50.0		7.8
313.15	30.0	51	52	413.15	0.10	3.68	
313.15	40.0	56	57	413.15	10.0	3.97	
333.15	0.10	18.6	19.5	413.15	20.0	4.35	
333.15	10.0	20.7	21.8	413.15	30.0	4.64	
333.15	20.0	23.1	24.0	413.15	40.0	5.0	
333.15	30.0	25.3	26.4	433.15	0.10	2.86	3.05
333.15	40.0	27.9	29.1	433.15	10.0	3.11	3.24
343.15	0.10		14.9	433.15	20.0	3.33	3.52
353.15	0.10	11.0	11.4	433.15	40.0	3.83	4.09
353.15	10.0	12.1	12.7	433.15	50.0		4.34
353.15	20.0	13.4	13.8				

in Table 3. To represent the densities, ρ, the modified Tait equation[21] was used in the form

$$\{\rho(p) - \rho_r(p_r)\}/\rho(p) = C\,\lg\{(B + p)/(B + p_r)\} \tag{3}$$

where B is a function of temperature given by

$$B(T) = \sum_{i=0}^{2} b_i (T/\mathrm{K})^i \tag{4}$$

In eq 1, $p_r = 0.1$ MPa and $\rho_r(p_r)$ is the density listed in Table 1 that was represented by

$$\rho_r/\mathrm{kg{\cdot}m^{-3}} = \sum_{i=0}^{1} A_i (T/\mathrm{K})^i \tag{5}$$

with a standard deviation of the mean $100{\cdot}\sigma(\rho)/{<}\rho{>} = \pm\,0.027$ when the two parameters were $A_0 = 1640.32$ and $A_1 = -0.9032$.

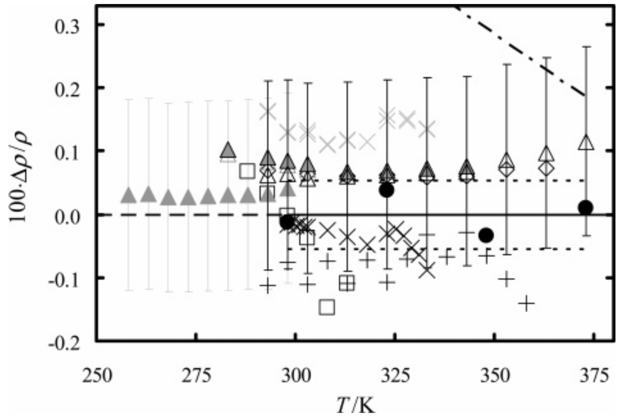

Figure 2. Relative deviations $\Delta\rho/\rho = \{\rho(\text{exptl}) - \rho(\text{calcd})\}/\rho(\text{calcd})$ of the experimentally determined density ρ(exptl) from the value obtained from eq 5 ρ(calcd) as a function of temperature T at $p = 0.1$ MPa for [hmim][Tf$_2$N]. ●, this work, sample A with w(H$_2$O) between (43 and 410)·10^{-6}; ◇, Earle and Seddon;[8] △, Widegren and Magee[1] with a vibrating tube densimeter within the Stabinger viscometer and w(H$_2$O) = 10^{-5}; □, Tokuda et al.;[10] +, Kato and Gmehling;[9] ×, Gomes de Azevedo et al.;[11] gray filled triangle, Widegren and Magee[1] with a vibrating tube densimeter within a Stabinger viscometer w(H$_2$O) = 10^{-5}; black outline gray filled triangle, Widegren and Magee[1] with a DSA5000 vibrating tube densimeter and w(H$_2$O) from (10 to 510)·10^{-6}; gray outline unfilled triangle, Widegren and Magee[1] with a DSA5000 vibrating tube densimeter and w(H$_2$O) from (10 to 870)·10^{-6}, -·-·-·-·-·-, Maginn;[6] and light gray ×, Esperanca et al.[12] The dashed line at $\Delta\rho/\rho = 0$ indicates an extrapolation of eq 5 to temperatures below our measurements to which the parameters of eq 5 were adjusted. The expanded uncertainty in our measurements is ± 0.3 %, and the dashed lines are $200{\cdot}\sigma(\rho)/{<}\rho{>} = 0.076$ of the standard deviation of the fit to eq 5, $\sigma(\rho)$.

Table 3. Electrical Conductivity κ of [hmim][Tf$_2$N] with Water Mass Fraction w(H$_2$O) between (90 and 180)·10^{-6} at Temperatures T and Pressure $p = 0.1$ MPa

T/K	κ/S·m^{-1}
278.15	0.077
283.15	0.102
288.15	0.135
293.15	0.172
298.15	0.217
303.15	0.268
308.15	0.327
313.15	0.390
323.15	0.54

The $\rho_r(p_r)$ obtained from eq 3 were combined with the densities of Table 1, to determine the adjustable parameters of eqs 3 and 4 with the results $b_0 = 415.953$ MPa, $b_1 = -1.3083$ MPa, $b_2 = 1.192{\cdot}10^{-3}$ MPa, and $C = 7.546{\cdot}10^{-2}$ that represented the data with $100{\cdot}\sigma(\rho)/{<}\rho{>} = \pm\,0.051$.

The ρ ($p = 0.1$ MPa) values reported by other workers[1,6,8−12] are shown as deviations from eq 5 in Figure 2, and in the overlapping temperature range, the literature values differ by ± 0.16 %, that is, within the assigned uncertainty. Extrapolating eq 5 to a temperature of 258 K, that is, 40 K below our measurements, provides estimates in agreement with the values reported by Widegren and Magee.[1] However, the smoothing equation for density reported by Maginn[6] differs from eq 5 by ≈ 0.6 % at $T = 283$ K and the difference decreases with increasing temperature to be ≈ 0.2 % at $T = 373$ K; only the differences within the ordinate are shown in Figure 2. At $p >$ 0.1 MPa, the densities from Table 1 and those reported by Gomes de Azevedo et al.[11] and Esperanca et al.[12] are shown relative to the smoothing eqs 3, 4, and 5 in Figure 2. All differences shown in Figure 3 are within the expanded uncertainty of our measurements of ± 0.3 %.

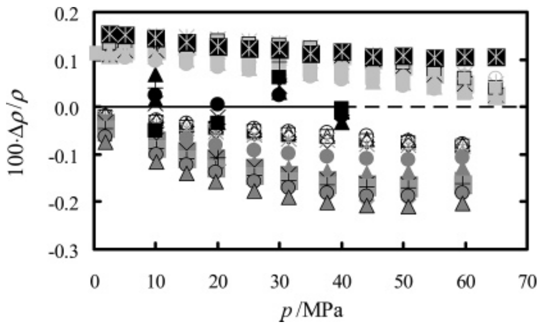

Figure 3. Relative deviations $\Delta\rho/\rho = \{\rho(\text{exptl}) - \rho(\text{calcd})\}/\rho(\text{calcd})$ of the experimentally determined density $\rho(\text{exptl})$ from the value obtained from eqs 3, 4, and 5 $\rho(\text{calcd})$ as a function of pressure p for [hmim][Tf$_2$N]. This work was performed with sample A with $w(H_2O)$ between $(43 \text{ and } 410)\cdot 10^{-6}$: ●, this work, $T = 298$ K; ▲, this work, $T = 323$ K; ■, this work, $T = 348$ K; ◆, this work, $T = 373$ K; ×, this work, $T = 398$ K; +, this work, $T = 423$ K; ○, ref 11, $T = 298$ K; △, ref 11, $T = 299$ K; □, ref 11, $T = 300$ K; ◇, ref 11, $T = 301$ K; dark gray cross, ref 11, $T = 302$ K; dark gray plus, ref 11, $T = 303$ K; dark gray filled circle, ref 11, $T = 308$ K; dark gray filled triangle, $T = 313$ K; dark gray filled square, ref 11, $T = 318$ K; dark gray filled diamond, ref 11, $T = 323$ K; black cross with dark gray square background, ref 11, $T = 325$ K; black plus with dark gray square background, ref 11, $T = 327$ K; dark gray filled circle with black outline, ref 11, $T = 329$ K; dark gray filled triangle with black outline, ref 11, $T = 331$ K; dark gray filled square with black outline, ref 11, $T = 333$ K; light gray asterisk within a black filled square, ref 12, $T = 293$ K; light gray filled circle, ref 12, $T = 298$ K; light gray plus, ref 12, $T = 303$ K; light gray filled circle, ref 12, $T = 308$ K; light gray filled triangle, ref 12, $T = 313$ K; light gray filled square, ref 12, $T = 318$ K; light gray asterisk, ref 12, $T = 328$ K; light gray filled square with black outline, ref 12, $T = 333$ K; and black asterisk with light gray square background, ref 12, $T = 338$ K. The dashes at $\Delta\rho/\rho = 0$ indicate an extrapolation of eqs 3, 4, and 5 to pressures above our measurements to which the parameters of eqs 3, 4, and 5 were adjusted. The expanded uncertainty in our measurements is ± 0.3 %.

Using the rule of Vogel,[22] the viscosities η ($p = 0.1$ MPa) listed in Table 2 for sample B were represented by

$$\eta_0/\text{mPa}\cdot\text{s} = \exp[e + f/\{g + (T/\text{K})\}] \qquad (6)$$

with $100\cdot\sigma(<\eta>)/\eta = 0.1$ when the constants were adjusted to be $e = -2.085$, $f = 868.689$, and $g = -161.226$. The relative deviations of the measurements from eq 6 for sample A are, as shown in Figure 4, systematically below those of B by about 5 %, that is, 2.5 times the combined estimated expanded uncertainty. This is not surprising because $w(H_2O, \text{A}) > w(H_2O, \text{B})$. The η ($p = 0.1$ MPa) values reported by other workers[5,1,6,7] are also shown in Figure 4 and differ from eq 6 by ± 5 % including the values reported by Maginn[6] with $w(H_2O) = 30\cdot 10^{-6}$. Indeed, the agreement between the results obtained from different techniques and sources of systematic error on samples of different water mass fractions that varied, when cited, from $(7 \text{ to } 870)\cdot 10^{-6}$ is considered remarkable.

Widegren and Magee[1] report measurements of viscosity, obtained with an Ubbelohde capillary viscometer, as a function of $w(H_2O)$ from $(10 \text{ to } 8200)\cdot 10^{-6}$ at two temperatures of (293 and 298) K and provide $\mathrm{d}\eta(293\text{ K})/\mathrm{d}w(H_2O) = -3253$ mPa·s and $\mathrm{d}\eta(298\text{ K})/\mathrm{d}w(H_2O) = -2481$ mPa·s. These derivatives can be used to account for the difference in viscosity observed between samples A and B. To do so, the mass fraction of water while the sample was within the viscometer must be known. If the final water mass fractions are considered, the true values for samples A and B then the difference $\Delta w = w(\text{A}) - w(\text{B})$ is $293\cdot 10^{-6}$. At $T = 293$ K, this difference suggests the viscosity of sample A is about 1 % below that of sample B, while at $T = 298$ K, sample A is 0.8 % below B; both are within the assigned uncertainty. When these anticipated differences are accounted for, the measured viscosities of samples A and B agree within the combined expanded uncertainties. The difference also increases with increasing temperature which is consistent with the differences shown in Figure 4. An upper bound on the plausible difference in water mass fraction between samples A and B is $403\cdot 10^{-6}$ which decreases the differences in the viscosity of the samples by about 1.5 %, while the lower bound gives $\Delta w = 36\cdot 10^{-6}$ and results in viscosity differences that are a factor of about 8 less than for $\Delta w = 293\cdot 10^{-6}$. The values of $\mathrm{d}\eta/\mathrm{d}w(H_2O)$ also permit the estimation of the viscosity of dry [hmim][Tf$_2$N]: for sample A with $w(H_2O) = 410\cdot 10^{-6}$, the worst case, the viscosities reported at temperatures of (298 and 293) K are 1.6 % and 1.5 %, respectively, below the value for dry [hmim][Tf$_2$N].

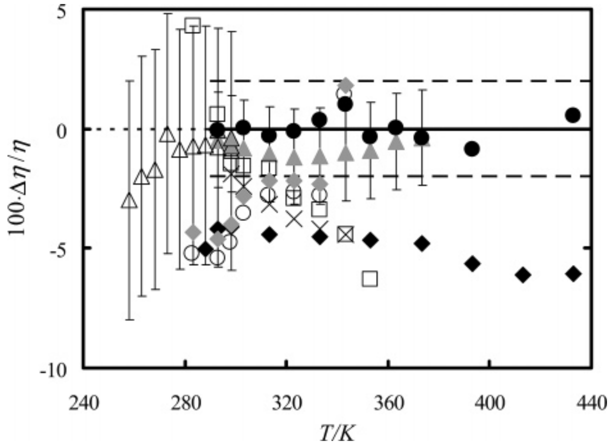

Figure 4. Relative deviations $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the experimentally determined viscosity $\eta(\text{exptl})$ from the value obtained from eq 6 $\eta(\text{calcd})$ as a function of temperature at $p = 0.1$ MPa for [hmim][Tf$_2$N]. ●, this work with $w(H_2O)$ from $(7 \text{ to } 117)\cdot 10^{-6}$; ◆, this work with $w(H_2O)$ from $(43 \text{ to } 410)\cdot 10^{-6}$; △, Widegren and Magee[1] with $w(H_2O) = 10^{-5}$ and a Stabinger viscometer; gray filled triangle, Widegren and Magee[1] with $w(H_2O) = 10^{-5}$ and a Stabinger viscometer; gray filled triangle with black border, Widegren and Magee[1] Ubbelohde capillary viscometer with $w(H_2O)$ of $(10 \text{ and } 20)\cdot 10^{-6}$; ○, Crosthwaite et al.;[1] □, Tokuda et al.;[10] ×, Nieto de Castro;[7] gray filled ◇, Maginn with $w(H_2O) = 30\cdot 10^{-6}$.[6] The dashed line at $100\cdot\Delta\eta/\eta = \pm 2$ is the expanded uncertainty in our measurements, while that at $100\cdot\Delta\eta/\eta = 0$ indicates an extrapolation of eq 6 to temperatures below our measurements to which the parameters were adjusted.

Table 4. Coefficients of Equation 1 Adjusted to Best Fit the Measurements of Viscosity Reported in Table 2 for Water Mass Fraction $w(H_2O)$ between $(7 \text{ and } 117)\cdot 10^{-6}$

a	b	c	d	e	T_0
−2.1114	0.003281	876.81	1.2576	−0.002902	160.58

The $\eta(T, p)$ values of sample B with $p \geq 0.1$ MPa listed in Table 2 were fit by the empirical Vogel−Fulcher−Tammann (VFT) equation[22−24]

$$\eta(T,p)/\text{mPa}\cdot\text{s} = \exp\left\{a + b(p/\text{MPa}) + \frac{c + d(p/\text{MPa}) + e(p/\text{MPa})^2}{(T/\text{K}) - T_0}\right\} \qquad (7)$$

with $100\cdot\sigma(\eta)/<\eta> = \pm 0.44$, and the six parameters obtained are listed in Table 4. The viscosities listed in Table 1 for both samples A and B are shown in Figure 5 as relative deviations from eq 7 and, as expected, those for A, with a greater water mass fraction, lie systematically below eq 7 by 5 % but within 2.5 times the estimated expanded uncertainty. To our knowledge, there are no other measurements of the viscosity of [hmim]-

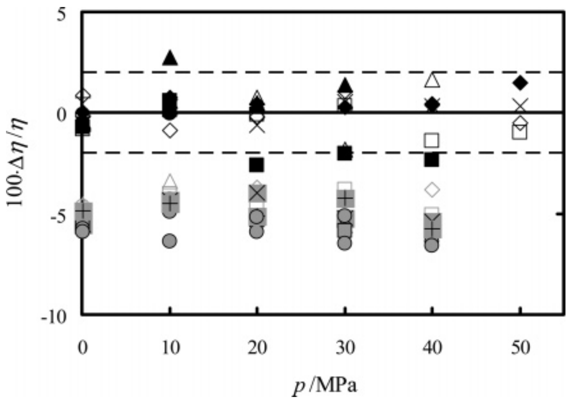

Figure 5. Relative deviations $\Delta\eta/\eta = \{\eta(\text{exppttl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the experimentally determined viscosity η(exptl) from the value η(calcd) obtained from eq 7 with coefficients of Table 3 as a function of pressure p for [hmim][Tf_2N]. This work with $w(H_2O)$ from (7 to 117)·10^{-6}: ●, $T = 293$ K; ▲, $T = 303$ K; ■, $T = 313$ K; ∗, $T = 323$ K; ◆, $T = 333$ K; +, $T = 343$ K; ×, $T = 353$ K; ○, $T = 363$ K; △, $T = 373$ K; □, $T = 393$ K; ◇, $T = 433$ K. This work with $w(H_2O)$ from (43 to 410))·10^{-6}: ∗ with gray square background, $T = 288$ K; gray outline unfilled circle, $T = 293$ K; gray outline unfilled triangle, $T = 298$ K; gray outline unfilled square, $T = 313$ K; gray outline unfilled diamond, $T = 333$ K; black cross with gray square background, $T = 353$ K; black plus with gray square background, $T = 373$ K; gray filled □, $T = 393$ K; gray filled ◇, $T = 413$ K; gray filled ○, $T = 433$ K. The dashed line is the expanded uncertainty in our measurements of ± 2 %.

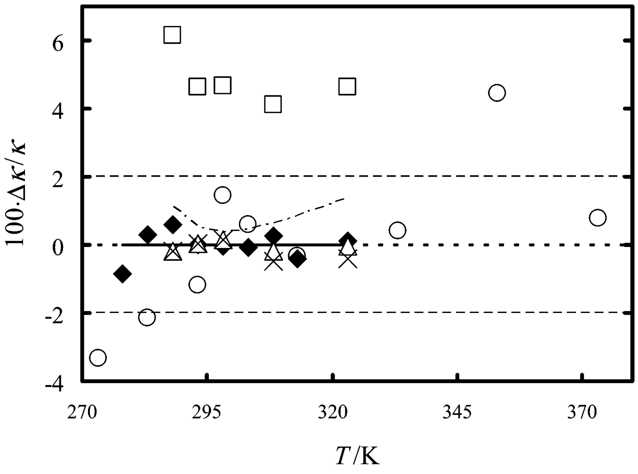

Figure 6. Relative deviations $\Delta\kappa/\kappa = \{\kappa(\text{exptl}) - \kappa(\text{calcd})\}/\kappa(\text{calcd})$ of the experimentally determined viscosity κ(exptl) from the value κ(calcd) obtained from eq 8 as a function of temperature T for [hmim][Tf_2N]. ◆, this work, with $w(H_2O)$ between (90 and 180)·10^{-6}; ×, Widegren et al.;[13] △, Widegren and Magee[1] with $w(H_2O) = 10\cdot10^{-6}$; □, Widegren and Magee[1] with $w(H_2O) = 940\cdot10^{-6}$, $T = 393$ K; ○, Tokuda et al.;[10] —·—·, correlation reported by Widegren and Magee[1] with the same functional form as eq 8. The dashed line at $100\cdot\Delta\kappa/\kappa = \pm 2$ is the expanded uncertainty in our measurements, while that at $100\cdot\Delta\kappa/\kappa = 0$ indicates an extrapolation of eq 8 to temperatures outside our measurements to which the parameters were adjusted.

[Tf_2N] at $p > 0.1$ MPa to compare with the results from Table 2 or eq 7.

The nine measurements of electrical conductivity κ listed in Table 3 were represented by

$$\kappa/(\text{S}\cdot\text{m}^{-1}) = \sum_{j=0}^{2} a_j(T/\text{K} - 273.15)^j \qquad (8)$$

with a standard deviation of $100\cdot\sigma(\kappa)/\langle\kappa\rangle = \pm 0.34$ when the parameters were adjusted to be $a_0 = 5.8969\cdot10^{-2}$, $a_1 = 2.9954\cdot10^{-3}$, and $a_2 = 1.3285\cdot10^{-4}$. The κ listed in Table 3 are shown in Figure 6 as fractional deviations from eq 8 along with those reported by other workers.[6,10,13] In the temperature range that overlaps the values listed in Table 3, the conductivities reported by Widegren and Magee,[1] with $w(H_2O) = 10\cdot10^{-6}$, Widegren et al.,[13] and Tokuda et al.[10] differ from eq 8 by less than the estimated expanded uncertainty of the measurements reported here. Not surprisingly, the conductivities reported by Widegren and Magee[1] with $w(H_2O) = 940\cdot10^{-6}$ lie systematically above the values from eq 8 by about 5 %. Extrapolation of our results to a temperature of 273 K, 5 K below our lowest experimental temperature, provides a value of about 3.3 % above the measurement of Tokuda et al.,[10] while extrapolation of eq 8 to (333, 353, and 373) K, the estimates differ by (−0.3, 4.5, and 1.7) % from those of ref 10. This agreement is remarkable given the extrapolation of 50 K from the highest temperature of our measurements of $T = 323$ K, and this extrapolation is equivalent to the temperature range of our measurements; no particular interpretation should be placed on this agreement which is, in the absence of other measurements, considered fortuitous. The correlation of the κ reported by Widegren et al.,[13] which is identical in form to eq 8 and based solely on their measurements, when extrapolated to $T = 273$ K differs from the results of Tokuda et al.[10] by −12 % (about 3 times the difference from eq 8), while at higher temperatures the differences are within ± 2.5 %.

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Literature Cited

(1) Widegren, J. A.; Magee, J. W. Density, Viscosity, Speed of Sound, and Electrolytic Conductivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Its Mixtures with Water. *J. Chem. Eng. Data* manuscript number je-2007-00329a, accepted for publication August 23, 2007.

(2) Widegren, J. A.; Laesecke, A.; Magee, J. W. The effect of dissolved water on the viscosities of hydrophobic room-temperature ionic liquds. *Chem. Commun.* **2005**, 1610−1612.

(3) http://www.iupac.org/projects/2002/2002-005-1-100.html.

(4) Blokin, A. V.; Paulechka, Y. U.; Kabo, G. J. Thermodynamic Properties of [C6mim][NTf2] in the Condensed State. *J. Chem. Eng. Data* **2006**, *51*, 1377−1388.

(5) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase Transition and Decomposition Temperatures, Heat Capacities and Viscosities of Pyridinium Ionic Liquids. *J. Chem. Thermodyn.* **2005**, *37*, 559−568.

(6) Maginn, E. J. *Design and Evaluation of Ionic Liquids as Novel CO_2 Absorbents*; Technical Report for for Dept. of Energy Award DE-FG26-04NT42122, Jan. 31, 2005.

(7) Santos, F. J. V.; Ribeiro, A. P.; Nieto de Castro, C. *Viscosity of 1-Hexyl-3-Methylimidazolium Bis(Trifluorosulfonyl)Imide, [HMIM]-[TF2N]*, Proceedings of the Asian Thermophysical Properties Conference 21−24, August, 2007, Fukuoka, Japan; Paper No. 263.

(8) Earle, M. J.; Seddon, K. R. Ionic Liquids. Green Solvents for the Future. *Pure Appl. Chem.* **2000**, *72*, 1391−1398.

(9) Kato, R.; Gmehling, J. Systems with ionic liquids: Measurement of VLE and γ^{∞} data and prediction of their thermodynamic behavior using original UNIFAC, mod. UNIFAC(Do) and COSMO-RS(Ol). *J. Chem. Thermodyn.* **2005**, *37*, 603−619.

(10) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How Ionic are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 19593−19600.

(11) Gomes de Azevedo, R.; Esperanca, J. M. S. S.; Szydlowski, J.; Visak, Z. P.; Pires, P. F.; Guedes, H. J. R.; Rebelo, L. P. N. Thermophysical and Thermodynamic Properties of Pure Ionic Liquids over an Extended Pressure Range: [bmim][NTf_2] and [hmim][NTf_2]. *J. Chem. Thermodyn.* **2005**, *37*, 888−899.

(12) Esperança, J. M. S. S.; Henrique J. R. Guedes, H. J. R.; Lopes, J. N. C.; Rebelo, L. P. N. The pressure−density−temperature ($p-\rho-T$) surface of [C_6mim][NTf_2]. *J. Chem. Eng. Data*, submitted, 2007.

(13) Widegren, J. A.; Saurer, E.; Marsh, K. N.; Magee, J. W. Electrolytic conductivity of four imidazolium-based room-temperature ionic liquids and the effect of a water impurity. *J. Chem. Thermodyn.* **2005**, *37*, 569−575.

(14) Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. Vibrating Wire Viscometer with Wire Diameters of (0.05 and 0.15) mm: Results for Methylbenzene and Two Fluids with Nominal Viscosities at T = 298 K and p = 0.01 MPa of (14 and 232) mPa·s at Temperatures between (298 and 373) K and Pressures below 40 MPa. *J. Chem. Eng. Data* **2005**, *50*, 647−655.

(15) Kurihara, K.; Kandil, M. E.; Marsh, K. N.; Goodwin. A. R. H. Measurement of the Viscosity of Liquid Cyclopentane Obtained with a Vibrating Wire Viscometer at Temperatures between (273 and 353) K and Pressures below 45 MPa. *J. Chem. Eng. Data* **2007**, *52*, 803−807.

(16) Al Motari, M. M.; Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. Density and Viscosity of Diisodecyl Phthalate $C_6H_4(COOC_{10}H_{21})_2$, with Nominal Viscosity at T = 298 K and p = 0.1 MPa of 87 mPa·s, at Temperatures from (298.15 to 423.15) K and Pressures up to 70 MPa. *J. Chem. Eng. Data* **2007**, *52*, 1233−1239.

(17) Kandil, M. E.; Harris, K. R.; Goodwin, A. R. H.; Hsu, K.; Marsh, K. N. Measurement of the Viscosity and Density of a Reference Fluid, with Nominal Viscosity at $T = 298$ K and $p = 0.1$ MPa of 29 mPa·s, at Temperatures Between (273 and 423) K and Pressures below 275 MPa. *J. Chem. Eng. Data* **2006**, *51*, 2185−2196.

(18) Lundstrum, R.; Goodwin, A. R. H.; Hsu, K.; Frels, M.; Caudwell, D. R.; Trusler, J. P. M.; Marsh, K. N. Measurement of the Viscosity and Density of Two Reference Fluids, with Nominal Viscosities at $T =$ 298 K and $p = 0.01$ MPa of (16 and 29) mPa·s, at Temperatures between (298 and 393) K and Pressures below 55 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1377−1388.

(19) Sopkow, T.; Goodwin, A. R. H.; Hsu, K. Vibrating Wire Viscometer with Nominal Wire Diameter of 0.15 mm: Measurement of The Viscosity of Two Certified Reference Fluids, with Nominal Viscosities at $T = 298$ K and $p = 0.1$ MPa of (16 and 29) mPa·s, at Temperatures Between (298 and 353) K and Pressures Below 55 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1732−1735.

(20) Robinson R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959; p 462.

(21) Hayward, A. T. J. Compressibility equations for liquids: a comparative study. *Br. J. Appl. Phys.* **1967**, *18*, 965−977.

(22) Vogel, H. The law of the relation between the viscosity of liquids and the temperature. *Phys. Z* **1921**, *22*, 645−646.

(23) Fulcher, G. S. Analysis of recent measurements of the viscosity of glasses. *Am. Ceram. Soc. J.* **1925**, *8*, 339−355.

(24) Tammann, G.; Hesse, W. Die Abhängigkeit der Viscosität von der Temperatur bei unterkühlten Flüssigkeiten. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245−257.

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