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# Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Methyl-3-octylimidazolium Hexafluorophosphate and 1-Methyl-3-octylimidazolium Tetrafluoroborate

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The viscosities of the ionic liquids 1-methyl-3-octylimidazolium hexafluorophosphate, [OMIM]$PF_6$, and 1-methyl-3-octylimidazolium tetrafluoroborate [OMIM]$BF_4$, have been measured between (0 and 80) °C and at pressures to 176 MPa ([OMIM]$PF_6$) and 224 MPa ([OMIM]$BF_4$) with a falling-body viscometer. The overall uncertainty is estimated at ± (2 to 3) %. Modified Litovitz and Vogel−Fulcher−Tammann equations are used to represent the temperature and pressure dependence. The $T_0$ parameter for the latter is found to be consistent with Angell's relationship linking $T_0$ and the strength parameter $D$ with the glass temperature $T_g$. Densities between (0 and 90) °C at atmospheric pressure are also reported for both substances. These have an overall uncertainty estimated at ± 0.00005 g·cm$^{-3}$. The in-built viscosity correction for the Anton-Paar DMA5000 densimeter was confirmed using high-viscosity reference standards to an upper limit of 16 Pa·s.

## Introduction

This work continues a series on the transport properties of ionic liquids at high pressure. There is currently great interest in ionic liquids for their favorable solvent and electrochemical properties; their potential, in favorable circumstances, as replacements for traditionally used industrial organic solvents; and their use in biphasic catalysis and the electro-winning of metals.[1] Hence it is important that reliable thermophysical data and property databases of these materials be available for efficient design of processes and plant. Despite (or perhaps because of) the complex interactions (electrostatic, van der Waals, and H-bonding) between the component ions, ionic liquids are also of interest in the development of theoretical models of electrolytes as the liquid region is much more readily accessible to experiment than for simple inorganic salts. Determination of the transport properties (viscosity, ionic conductivity, and ion self-diffusion coefficients) allows analysis of correlations between ionic velocities, and it is important that the measurements be precise and accurate. High-pressure data, in principle, allow the separation of volume effects from those of temperature. This paper forms one element of a program of systematic thermophysical property measurements for representative ionic liquids.

Here we report viscosities for two members of one of the most commonly studied ionic liquid groups, that based on imidazolium-containing cations, namely, 1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM]$PF_6$ or [$C_8$-mim]$PF_6$) and 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM]$BF_4$ or [$C_8$-mim]$BF_4$). The choice has also been influenced by the availability of *pVT* data necessary for measurements made with a falling-body viscometer. These new measurements supplement our earlier ones on 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]$PF_6$ or [$C_4$-mim]$PF_6$),[2] allowing the comparison of pairs of ionic liquids with either a common cation ([OMIM]$^+$) or a common anion ($PF_6^-$). Densities were also measured at atmospheric pressures with an Anton-Paar DMA5000 vibrating tube densimeter, and we have tested the range of validity of the viscosity correction for this instrument, extending it to 16 Pa·s.

## Experimental Section

Two separate [OMIM]$PF_6$ samples (designated OP1 and OP2 in the tables) and one of [OMIM]$BF_4$ (sample OB1) were prepared in a manner similar to [BMIM]$PF_6$.[3] Care was taken to remove chloride: any residual amount was less than the detection limit of elemental titration analysis (mass fraction $10^{-4}$) The molar masses were taken as (340.289 and 282.129) g·mol$^{-1}$, respectively.

Imidazolium-containing ionic liquids are hygroscopic, and as with most ionic liquids, the physical properties are very sensitive to the presence of small amounts of water.[3−6] These liquids, particularly the hexafluorophosphates, can attack glass at temperatures above 70 °C in the presence of traces of water. Hence we have taken care to minimize exposure to water in handling the samples. The water contents of OP2 and OB1 were determined by Karl Fischer titration to be ((27 ± 4) and (54 ± 10)·$10^{-6}$) mass fraction, respectively, prior to their vacuum sealing in glass ampules and their shipment from Sendai to Canberra where the density and viscosity measurements were made. The water contents of OP1 and the [BMIM]$PF_6$ sample reported on previously,[2] though not measured, are estimated to lie within the same range. The ionic liquid ampules were warmed to about 75 °C to increase the sample fluidity and opened inside a glovebox with the atmosphere dried with either phosphorus pentoxide or concentrated sulfuric acid. The oven-dried viscometer sample tube was then filled and sealed within the glovebox. The sample tube was then inserted into the pressure vessel. Contrary to our usual practice, the ionic liquids

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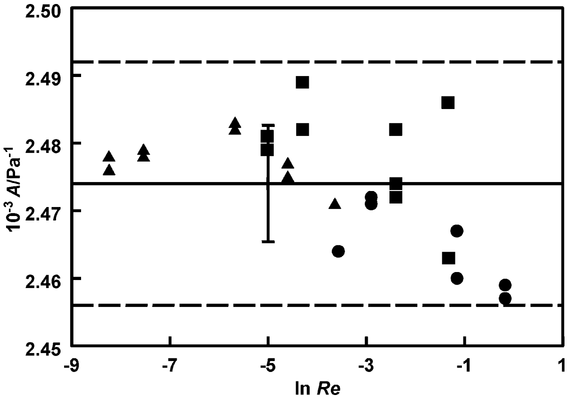

**Figure 1.** Viscometer calibration constant, *A*, for Cannon certified reference oils, (20 to 50) °C. $A = (2.474 \pm 0.009)\ 10^3\ \mathrm{Pa}^{-1}$. Symbols: ●, N100; ■, S200; and ▲, N1000. The dashed lines represent the expanded uncertainty of fit or 95 % confidence limits.

**Table 1. Test of the Viscosity Correction for the Anton-Paar DMA5000 Densimeter Using Cannon Reference Fluid N4000**

| $\theta$ | $\eta$ | $\rho_{\mathrm{uncorr}}$ | $\rho_{\mathrm{corr}}{}^{a}$ | $\rho_{\mathrm{uncorr}}-\rho_{\mathrm{corr}}$ | $\rho^{b}$ |
|---|---|---|---|---|---|
| °C | mPa·s | g·cm$^{-3}$ | g·cm$^{-3}$ | g·cm$^{-3}$ | g·cm$^{-3}$ |
| 20 | 16 174 | 0.883 99 | 0.883 37 | 0.000 17 | 0.8832 ± 0.0002 |
| 25 | 10 242 | 0.881 17 | 0.880 56 | 0.000 16 | 0.8804 ± 0.0002 |
| 40 | 2 966 | 0.872 74 | 0.872 13 | 0.000 13 | 0.8720 ± 0.0002 |
| 50 | 1 444 | 0.867 15 | 0.866 54 | 0.000 14 | 0.8664 ± 0.0002 |
| 60 | 756 | 0.861 55 | 0.860 95 | 0.000 15 | 0.8608 ± 0.0001 |

[a] Uncertainty ± 0.000 05 g·cm$^{-3}$. [b] As given by Cannon.

**Table 2. Parameters for Tait (*ln* form) and Hayward Equations of State**

| | [OMIM]BF$_4$ | | [OMIM]PF$_6$ | |
|---|---|---|---|---|
| *T*/°C | 25 | 50 | 25 | 50 |
| *B*/MPa | 125.22 | 90.62 | 183.84 | 190.58 |
| *C* | 0.062 20 | 0.054 45 | 0.081 33 | 0.093 56 |
| $\delta\rho$/%$^a$ | 0.2 | 0.1 | 0.1 | 0.1 |

| | [OMIM]BF$_4$ | [OMIM]PF$_6$ |
|---|---|---|
| $\alpha_{00}$/MPa | −1618.54 | −445.350 |
| $\alpha_{01} \times 10^3$/(MPa·K) | 1091.09 | 817.894 |
| $\alpha_{10}$ | 10.6362 | −4.616 60 |
| $\alpha_{11}$/K | −1172.86 | 2935.64 |
| $\delta\rho$/%$^a$ | 0.1 | 0.1 |

[a] Standard uncertainty of fit to the density.

were not filtered during the filling of the viscometer due to the possibility of reaction with the glass sinter at the loading temperature; however, filtration is part of the preparation procedure.[3]

The falling body viscometer employed and its operation have been described previously.[2] The working equation is

$$\eta(p,T) = \frac{t(1 - \rho/\rho_s)}{A[(1 + 2\alpha(T - T_{\mathrm{ref}})][1 - 2\beta(p - p_{\mathrm{ref}})/3]} \tag{1}$$

where $\eta$ is the shear viscosity, *t* is the fall time, $\rho$ is the density of the fluid, $\rho_s$ is the density of the sinker, α is the coefficient of thermal expansion, and $\beta$ is the bulk compressibility of the sinker and tube material, in this case 316 stainless steel. *A* is the calibration constant. The sinker densities were corrected for changes in *T* and *p* from the reference state point, $T_{\mathrm{ref}} = 298.15$ K and $p_{\mathrm{ref}} = 0.1$ MPa using the relation:

$$\rho_s = \frac{\rho_s(T_{\mathrm{ref}},p_{\mathrm{ref}})}{[1 + 3\alpha(T - T_{\mathrm{ref}})][1 - \beta(p - p_{\mathrm{ref}})]} \tag{2}$$

**Table 3. Density $\rho$ of [OMIM]BF$_4$ from $\theta$ = (0 to 90) °C**

| $\theta$/°C | $\rho$/g·cm$^{-3}$ | $\theta$/°C | $\rho$/g·cm$^{-3}$ | $\theta$/°C | $\rho$/g·cm$^{-3}$ | $\theta$/°C | $\rho$/g·cm$^{-3}$ |
|---|---|---|---|---|---|---|---|
| 0 | 1.120 96 | 20 | 1.107 11 | 40 | 1.093 37 | 80 | 1.066 60 |
| 5 | 1.117 48 | 20 | 1.107 11 | 50 | 1.086 56 | 90 | 1.060 08 |
| 10 | 1.114 01 | 25 | 1.103 68 | 60 | 1.079 83 | | |
| 15 | 1.110 55 | 30 | 1.100 24 | 70 | 1.073 18 | | |

**Table 4. Density $\rho$ of [OMIM]PF$_6$ from $\theta$ = (0 to 90) °C**

| $\theta$/°C | $\rho$/g·cm$^{-3}$ | $\theta$/°C | $\rho$/g·cm$^{-3}$ |
|---|---|---|---|
| | Sample OP1 | | |
| 0 | 1.256 13 | 40 | 1.225 34 |
| 5 | 1.252 25 | 50 | 1.217 70 |
| 10 | 1.248 38 | 60 | 1.210 29 |
| 15 | 1.244 52 | 70 | 1.202 88 |
| 20 | 1.240 68 | 80 | 1.195 49 |
| 25 | 1.236 84 | 90 | 1.188 13 |
| 30 | 1.233 01 | | |
| | Sample OP2 | | |
| 25 | 1.236 75 | 50 | 1.217 68 |

The viscometer tube diameter is 6.52 mm, and that of the sinker is 6.0 mm. The Reynolds number for annular flow in a viscometer of this type is given by

$$Re = 2r_1{}^2\rho v/((r_2 - r_1)\eta) \tag{3}$$

where *v* is the terminal velocity of the sinker and $r_1$ and $r_2$ are the radii of the sinker and tube, respectively.

The previous calibration[2] was extended using Cannon viscosity standards N100, S200. and N1000 (Lot Nos. 03501, 04201,

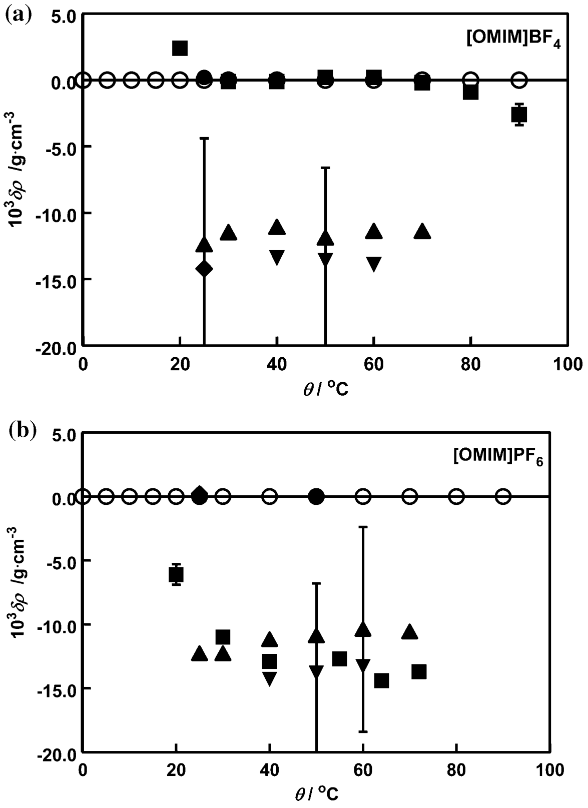

**Figure 2.** (a) Residuals (experimental − calculated values) for the fit of the experimental atmospheric pressure and literature densities for [OMIM]-BF$_4$ to eq 6a as a function of temperature, $\theta$. Symbols: ○, this work; ▲, ref 7; ▼, ref 10; ■, ref 11; ◆, ref 12; ●, ref 13. (b) Residuals (experimental − calculated values) for the fit of the experimental atmospheric pressure and literature densities for [OMIM]PF$_6$ to eq 6b as a function of temperature, $\theta$. Symbols: ○, this work, sample OP1; ●, this work, sample OP2; ▲, ref 7; ▼, ref 10; ■, ref 11; ◆, ref 14.

**Table 5. Viscosity $\eta$ of [OMIM]BF$_4$ from $\theta$ = (0 to 80) °C and $p$ = (0.1 to 224) MPa**

| $\theta$ / °C | $t$ / s | $p$ / MPa | $V$ / cm$^3$·mol$^{-1}$ | $\rho$ / g·cm$^{-3}$ | $\eta$ / mPa·s | $Re$ |
|---|---|---|---|---|---|---|
| 0.00 | 6691 | 0.1 | 251.68 | 1.12096 | 2291 | 0.0005 |
| 0.00 | 6686 | 0.1 | 251.68 | 1.12096 | 2289 | 0.0005 |
| 5.00 | 4313 | 0.1 | 252.47 | 1.11748 | 1477 | 0.0012 |
| 5.00 | 4314 | 0.1 | 252.47 | 1.11748 | 1478 | 0.0012 |
| 10.00 | 2868 | 0.1 | 253.25 | 1.11401 | 982 | 0.0027 |
| 10.00 | 2867 | 0.1 | 253.25 | 1.11401 | 982 | 0.0027 |
| 15.00 | 1964 | 0.1 | 254.04 | 1.11055 | 673 | 0.0058 |
| 15.00 | 1964 | 0.1 | 254.04 | 1.11055 | 673 | 0.0058 |
| 20.00 | 1381 | 0.1 | 254.83 | 1.10711 | 473 | 0.012 |
| 20.00 | 1380 | 0.1 | 254.83 | 1.10711 | 473 | 0.012 |
| 25.00 | 994.6 | 0.1 | 255.63 | 1.10368 | 341 | 0.023 |
| 25.00 | 1147 | 11.2 | 254.29 | 1.10948 | 393.0 | 0.017 |
| 25.00 | 1390 | 26.2 | 252.61 | 1.11683 | 475.7 | 0.012 |
| 25.00 | 1868 | 50.5 | 250.21 | 1.12756 | 638.3 | 0.007 |
| 25.00 | 1890 | 51.5 | 250.12 | 1.12798 | 645.9 | 0.006 |
| 25.00 | 2109 | 60.8 | 249.29 | 1.13173 | 720.1 | 0.0052 |
| 25.00 | 2646 | 80.2 | 247.68 | 1.13907 | 902.3 | 0.0033 |
| 25.00 | 3317 | 100.2 | 246.19 | 1.14596 | 1130 | 0.0021 |
| 25.00 | 3993 | 116.7 | 245.07 | 1.15121 | 1359 | 0.0015 |
| 25.00 | 4027 | 117.5 | 245.02 | 1.15147 | 1371 | 0.0014 |
| 30.00 | 732.0 | 0.1 | 256.42 | 1.10024 | 251 | 0.041 |
| 30.00 | 730.2 | 0.1 | 256.42 | 1.10024 | 251 | 0.042 |
| 35.00 | 549.0 | 0.1 | 257.23 | 1.09678 | 188.4 | 0.073 |
| 35.00 | 548.4 | 0.1 | 257.23 | 1.09678 | 188.2 | 0.074 |
| 35.00 | 548.8 | 0.1 | 257.23 | 1.09678 | 188.3 | 0.073 |
| 35.00 | 549.9 | 0.1 | 257.23 | 1.09678 | 188.7 | 0.073 |
| 35.00 | 549.2 | 0.1 | 257.23 | 1.09678 | 188.5 | 0.073 |
| 35.00 | 553.9 | 0.8 | 257.13 | 1.09721 | 190.1 | 0.072 |
| 35.00 | 568.1 | 2.9 | 256.86 | 1.09838 | 194.9 | 0.069 |
| 35.00 | 586.5 | 5.6 | 256.51 | 1.00281 | 204.3 | 0.058 |
| 35.00 | 624.7 | 10.9 | 255.84 | 1.10276 | 214.2 | 0.057 |
| 35.00 | 744.9 | 26.0 | 254.06 | 1.11048 | 255.1 | 0.040 |
| 35.00 | 986.1 | 50.7 | 251.50 | 1.12180 | 337.1 | 0.023 |
| 35.00 | 1301 | 76.2 | 249.22 | 1.13205 | 444.0 | 0.014 |
| 35.00 | 1676 | 100.3 | 247.35 | 1.14061 | 571.1 | 0.008 |
| 35.00 | 2149 | 124.4 | 245.69 | 1.14829 | 731.7 | 0.005 |
| 35.00 | 2781 | 150.2 | 244.13 | 1.15563 | 945.5 | 0.003 |
| 35.00 | 4500 | 200.1 | 241.59 | 1.16779 | 1527 | 0.001 |
| 40.00 | 419.7 | 0.1 | 258.03 | 1.09337 | 144.1 | 0.13 |
| 50.00 | 258.3 | 0.1 | 259.65 | 1.08656 | 88.8 | 0.33 |
| 50.00 | 258.1 | 0.1 | 259.65 | 1.08656 | 88.7 | 0.33 |
| 50.00 | 258.1 | 0.1 | 259.65 | 1.08656 | 88.7 | 0.33 |
| 50.00 | 259.7 | 0.7 | 259.57 | 1.08689 | 89.2 | 0.32 |
| 50.00 | 272.3 | 4.9 | 259.01 | 1.08925 | 93.5 | 0.30 |
| 50.00 | 289.3 | 10.5 | 258.29 | 1.09228 | 99.3 | 0.26 |
| 50.00 | 340.1 | 25.8 | 256.39 | 1.01271 | 118.2 | 0.17 |
| 50.00 | 438.8 | 50.8 | 253.52 | 1.11283 | 150.1 | 0.12 |
| 50.00 | 560.0 | 75.7 | 250.91 | 1.12441 | 191.2 | 0.073 |
| 50.00 | 709.2 | 100.6 | 248.52 | 1.13522 | 241.8 | 0.046 |
| 50.00 | 890.6 | 125.5 | 246.33 | 1.14530 | 303.1 | 0.029 |
| 50.00 | 1108 | 149.9 | 244.36 | 1.15456 | 376.5 | 0.019 |
| 50.00 | 1384 | 175.5 | 242.44 | 1.16371 | 469.8 | 0.012 |
| 50.00 | 1703 | 199.8 | 240.75 | 1.17188 | 577.3 | 0.008 |
| 60.00 | 168.2 | 0.1 | 261.27 | 1.07983 | 57.8 | 0.77 |
| 60.00 | 168.2 | 0.1 | 261.27 | 1.07983 | 57.8 | 0.77 |
| 60.00 | 187.6 | 10.8 | 259.65 | 1.08655 | 64.4 | 0.62 |
| 60.00 | 217.5 | 25.7 | 257.64 | 1.09506 | 74.6 | 0.47 |
| 60.00 | 275.4 | 50.3 | 254.76 | 1.10743 | 94.3 | 0.30 |
| 60.00 | 347.4 | 75.6 | 252.28 | 1.11829 | 118.7 | 0.19 |
| 60.00 | 433.0 | 100.5 | 250.21 | 1.12755 | 147.7 | 0.12 |
| 60.00 | 535.7 | 125.3 | 248.43 | 1.13564 | 182.5 | 0.080 |
| 60.00 | 658.9 | 150.2 | 246.88 | 1.14276 | 224.3 | 0.054 |
| 60.00 | 806.8 | 175.1 | 245.52 | 1.14911 | 274.4 | 0.036 |
| 60.00 | 983.5 | 200.0 | 244.31 | 1.15478 | 334.1 | 0.024 |
| 70.00 | 114.5 | 0.1 | 262.89 | 1.07318 | 39.4 | 1.6 |
| 75.00 | 95.4 | 0.1 | 263.70 | 1.06990 | 32.8 | 2.4 |
| 75.00 | 95.2 | 0.3 | 263.66 | 1.07004 | 32.7 | 2.4 |
| 75.00 | 96.4 | 1.6 | 263.44 | 1.07095 | 33.2 | 2.3 |
| 75.00 | 97.9 | 3.1 | 263.18 | 1.07201 | 33.7 | 2.3 |
| 75.00 | 99.9 | 5.4 | 262.80 | 1.07353 | 34.4 | 2.2 |
| 75.00 | 104.6 | 10.2 | 262.03 | 1.07672 | 36.0 | 2.0 |
| 75.00 | 120.7 | 25.6 | 259.74 | 1.08619 | 41.4 | 1.5 |
| 75.00 | 150.3 | 50.3 | 256.66 | 1.09923 | 51.5 | 1.0 |
| 75.00 | 185.9 | 75.6 | 254.06 | 1.11048 | 63.6 | 0.65 |
| 75.00 | 227.6 | 100.5 | 251.91 | 1.11997 | 77.7 | 0.44 |
| 75.00 | 276.6 | 125.4 | 250.08 | 1.12815 | 94.3 | 0.30 |
| 75.00 | 335.7 | 150.4 | 248.50 | 1.13530 | 114.3 | 0.20 |
| 75.00 | 402.0 | 175.3 | 247.13 | 1.14160 | 136.8 | 0.14 |
| 75.00 | 481.2 | 200.2 | 245.93 | 1.14717 | 163.6 | 0.10 |
| 75.00 | 570.1 | 224.2 | 244.91 | 1.15198 | 193.7 | 0.07 |
| 80.00 | 81.8 | 0.1 | 264.51 | 1.06660 | 28.1 | 3.2 |

and 05201p, respectively) over the temperature range of (20 to 50) °C. These samples were filtered through a glass sinter (pore size (40 to 60) $\mu$m) prior to use. Excellent agreement within the experimental precision of 1 % was obtained, giving a calibration constant, $A = 2.474 \cdot 10^3$ Pa$^{-1}$ (standard uncertainty $0.009 \cdot 10^3$ Pa$^{-1}$) for the viscosity range of (51 to 2875) mPa·s and Reynolds number range of 0.0003 to 0.84 (see Figure 1).

Densities at atmospheric pressure were determined with an Anton-Paar DMA5000 vibrating-tube densimeter as described previously.[2] As before the glass vibrating-tube was carefully rinsed with filtered ethanol, acetone, and dry air before being loaded with ionic liquid. Previously we reported a test of the viscosity correction built in to the DMA5000 by using the Cannon reference fluid S200, which has a viscosity of 0.5848 Pa·s at 20 °C.[2] We have extended this test by using Cannon N4000, viscosity 16.174 Pa·s at 20 °C. The viscosity-corrected density agreed with that given by Cannon within the accuracy stated (Table 1). We believe this to be the most exacting test yet of the viscosity correction for this instrument.

Calculation of the viscosity from fall times requires knowledge of the density as a function of temperature and pressure. *pVT* data for [OMIM]BF$_4$ and [OMIM]PF$_6$ have been determined by Gu and Brennecke[7] at (25 and 50) °C. Gu and Brennecke fitted their data to the Tait equation of state but reported incorrect parameters. Corrected values are given in Table 2. As we needed again to extrapolate these *pVT* data to higher temperatures, they were used to calculate the linear secant modulus

$$\kappa = V_0 (p - p_0)/(V_0 - V) \tag{4}$$

as a function of temperature and pressure where $V_0$ is the molar volume at the saturation pressure $p_0$ for a given temperature $T$. $\kappa$ was fitted to the Hayward-type equation:[2]

$$\kappa = (\alpha_{00} + \alpha_{10}/T) + (\alpha_{01} + \alpha_{11}/T)p \tag{5}$$

The coefficients $\alpha_{ij}$ are also given in Table 2. High-pressure densities needed for the viscosity measurements were then calculated using our atmospheric pressure densities and eqs 4 and 5. As the sinker is 5 to 7 times denser than the ionic liquids used in this study, it is sufficient if the density is known to better than 5 % for an overall uncertainty in the viscosity of 1 % as it enters the viscosity calculation (eq 1) in terms of the buoyancy factor $(1 - \rho/\rho_s)$. The uncertainty in densities estimated from eq 5 is probably of the order of ± 0.5 %.

These ionic liquids are readily supercooled, and our results for [OMIM]PF$_6$ probably extend into the supercooled region. This was the case for [BMIM]PF$_6$[2] where we were able to determine both the density at 0 °C and the viscosity at 25 °C to 174 MPa although the freezing points at (0.1 and 55) MPa are (11.85 and 23.0) °C, respectively.[8] The melting points of [OMIM]PF$_6$ and [OMIM]BF$_4$ do not appear to have been

**Table 6. Viscosity $\eta$ of [OMIM]$PF_6$ from $\theta$ = (0 to 80) °C and $p$ = (0.1 to 176) MPa**

| $\theta$/°C | $t$/s | $p$/MPa | $V$/cm$^3$·mol$^{-1}$ | $\rho$/g·cm$^{-3}$ | $\eta$/mPa·s | *Re* | $\theta$/°C | $t$/s | $p$/MPa | $V$/cm$^3$·mol$^{-1}$ | $\rho$/g·cm$^{-3}$ | $\eta$/mPa·s | *Re* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Sample OP1 | | | | | | | |
| 50.00 | 470.4 | 0.1 | 279.45 | 1.2177 | 158 | 0.11 | 60.00 | 287.5 | 0.1 | 281.16 | 1.2103 | 96.8 | 0.30 |
| 50.00 | 470.0 | 0.1 | 279.45 | 1.2177 | 158 | 0.11 | 70.00 | 188.9 | 0.1 | 282.89 | 1.2029 | 63.6 | 0.69 |
| 50.00 | 473.1 | 0.1 | 279.45 | 1.2177 | 159 | 0.11 | 70.00 | 188.2 | 0.1 | 282.89 | 1.2029 | 63.4 | 0.70 |
| 50.00 | 474.0 | 0.1 | 279.45 | 1.2177 | 159 | 0.11 | 70.00 | 187.2 | 0.1 | 282.89 | 1.2029 | 63.1 | 0.71 |
| 50.00 | 660.7 | 26.3 | 276.13 | 1.2324 | 222 | 0.058 | 70.00 | 187.2 | 0.1 | 282.89 | 1.2029 | 63.1 | 0.71 |
| 50.00 | 881.5 | 49.9 | 273.42 | 1.2445 | 295 | 0.033 | 70.00 | 207.6 | 10.0 | 281.47 | 1.2090 | 69.8 | 0.58 |
| 50.00 | 1183 | 74.8 | 270.83 | 1.2565 | 395 | 0.019 | 80.00 | 128.6 | 0.1 | 284.64 | 1.1955 | 43.3 | 1.48 |
| 60.00 | 288.1 | 0.1 | 281.16 | 1.2103 | 97.0 | 0.30 | 80.00 | 128.8 | 0.1 | 284.64 | 1.1955 | 43.4 | 1.48 |
| | | | | | | Sample OP2 | | | | | | | |
| 0.00 | 19144 | 0.1 | 270.90 | 1.2561 | 6410 | 0.0001 | 50.00 | 1210 | 76.0 | 270.70 | 1.2570 | 404 | 0.018 |
| 5.00 | 11608 | 0.1 | 271.74 | 1.2522 | 3889 | 0.0002 | 50.00 | 1573 | 99.7 | 268.46 | 1.2676 | 525 | 0.011 |
| 10.00 | 7277 | 0.1 | 272.58 | 1.2484 | 2439 | 0.0005 | 60.00 | 290.9 | 0.1 | 281.16 | 1.2103 | 97.9 | 0.29 |
| 20.00 | 3175 | 0.1 | 274.27 | 1.2407 | 1065 | 0.003 | 60.00 | 290.7 | 0.1 | 281.16 | 1.2103 | 97.8 | 0.29 |
| 25.00 | 2189 | 0.1 | 275.13 | 1.2368 | 734 | 0.005 | 60.00 | 291 | 0.1 | 281.16 | 1.2103 | 97.9 | 0.294 |
| 25.00 | 2180 | 0.1 | 275.13 | 1.2368 | 732 | 0.005 | 60.00 | 291 | 0.1 | 281.16 | 1.2103 | 97.8 | 0.295 |
| 25.00 | 2546 | 10.2 | 273.94 | 1.2422 | 854 | 0.004 | 60.00 | 343 | 13.5 | 279.33 | 1.2182 | 115 | 0.21 |
| 25.00 | 3108 | 24.6 | 272.35 | 1.2494 | 1041 | 0.003 | 60.00 | 419 | 30.3 | 277.19 | 1.2276 | 141 | 0.14 |
| 25.00 | 3884 | 39.9 | 270.75 | 1.2568 | 1299 | 0.002 | 60.00 | 526 | 50.4 | 274.80 | 1.2383 | 176 | 0.092 |
| 30.00 | 1547 | 0.1 | 275.98 | 1.2330 | 519 | 0.011 | 60.00 | 689 | 75.1 | 272.09 | 1.2507 | 230 | 0.055 |
| 35.00 | 1115 | 0.1 | 276.85 | 1.2291 | 375 | 0.020 | 60.00 | 901 | 100.4 | 269.56 | 1.2624 | 301 | 0.032 |
| 35.00 | 1104 | 0.1 | 276.85 | 1.2291 | 371 | 0.021 | 60.00 | 1163 | 125.2 | 267.28 | 1.2731 | 387 | 0.020 |
| 35.00 | 1204 | 5.5 | 276.18 | 1.2321 | 404 | 0.018 | 70.00 | 189.1 | 0.1 | 282.89 | 1.2029 | 63.7 | 0.69 |
| 35.00 | 1282 | 9.9 | 275.65 | 1.2345 | 430 | 0.015 | 70.00 | 240.9 | 21.3 | 279.93 | 1.2156 | 81.0 | 0.43 |
| 35.00 | 1585 | 25.6 | 273.83 | 1.2427 | 531 | 0.010 | 70.00 | 336.3 | 51.8 | 276.06 | 1.2327 | 113 | 0.23 |
| 35.00 | 2141 | 48.4 | 271.39 | 1.2539 | 716 | 0.006 | 70.00 | 414.5 | 72.9 | 273.64 | 1.2436 | 139 | 0.15 |
| 35.00 | 3020 | 74.9 | 268.81 | 1.2659 | 1008 | 0.003 | 70.00 | 546.9 | 100.3 | 270.74 | 1.2569 | 183 | 0.087 |
| 40.00 | 823.9 | 0.1 | 277.71 | 1.2253 | 277 | 0.037 | 70.00 | 701.3 | 125.9 | 268.27 | 1.2685 | 234 | 0.054 |
| 50.00 | 473.4 | 0.1 | 279.45 | 1.2177 | 159 | 0.11 | 70.00 | 890.2 | 148.8 | 266.23 | 1.2782 | 296 | 0.034 |
| 50.00 | 648.1 | 24.8 | 276.31 | 1.2315 | 217 | 0.060 | 70.00 | 1139 | 175.9 | 263.99 | 1.2890 | 378 | 0.021 |

**Table 7. Coefficients of Best Fit for Equations 7 and 8**

| | coefficients and standard uncertainties | |
|---|---|---|
| | [OMIM]$BF_4$ | [OMIM]$PF_6$ |
| | Litovitz, eq 7 | |
| ln($A$/mPa·s) | −0.462 36 ± 0.004 15 | −0.538 65 ± 0.006 00 |
| $B \times 10^{-6}$/K$^3$ | 166.92 ± 0.11 | 189.29 ± 0.19 |
| standard uncertainty of fit | 0.5 % | 0.7 % |
| | VFT, eq 8 | |
| ln($A'$/mPa·s) | −3.16 72 ± 0.030 4 | −3.456 7 ± 0.053 8 |
| $B'$/K | 1283.52 ± 9.02 | 1407.98 ± 16.22 |
| $T_0$/K | 155.49 ± 0.51 | 158.03 ± 0.85 |
| $D^a$ | 8.25 | 8.91 |
| standard uncertainty of fit | 0.3 % | 0.6 % |

[a] Angell strength factor ($B'/T_0$).

determined as yet, although glass transition temperatures have been reported.[9] Freezing behavior was observed in some of our viscosity runs with [OMIM]$PF_6$ (e.g., near 100 MPa at 25 °C). Attempts to determine the freezing line by NMR relaxation time experiments were unsuccessful, due in part to the apparent similarity of the $T_1$ relaxation times in the liquid and solid phases (both proton and fluorine) and hysteresis effects.

## Results and Discussion

The density results at atmospheric pressure are presented in Tables 3 and 4 and can be represented by the polynomials

$$\rho([\text{OMIM}]\text{BF}_4)/\text{g}\cdot\text{cm}^{-3} = 1.121004 - 7.01436 \times 10^{-4}\,(\theta/°\text{C}) + 2.66725 \times 10^{-7}\,(\theta/°\text{C})^2 \quad (6a)$$

$$\rho([\text{OMIM}]\text{PF}_6)/\text{g}\cdot\text{cm}^{-3} = 1.256174 - 7.83151 \times 10^{-4}\,(\theta/°\text{C}) + 3.03073 \times 10^{-7}\,(\theta/°\text{C})^2 \quad (6b)$$

where $\theta$ is the Celsius temperature, with a standard uncertainty of (± 0.00003 and ± 0.00004) g·cm$^{-3}$ respectively. Figure 2 shows deviations of literature density data[7,10−14] for [OMIM]$BF_4$ and [OMIM]$PF_6$ from eqs 6. Error bars are given where the experimental precision is larger than the size of the symbols.

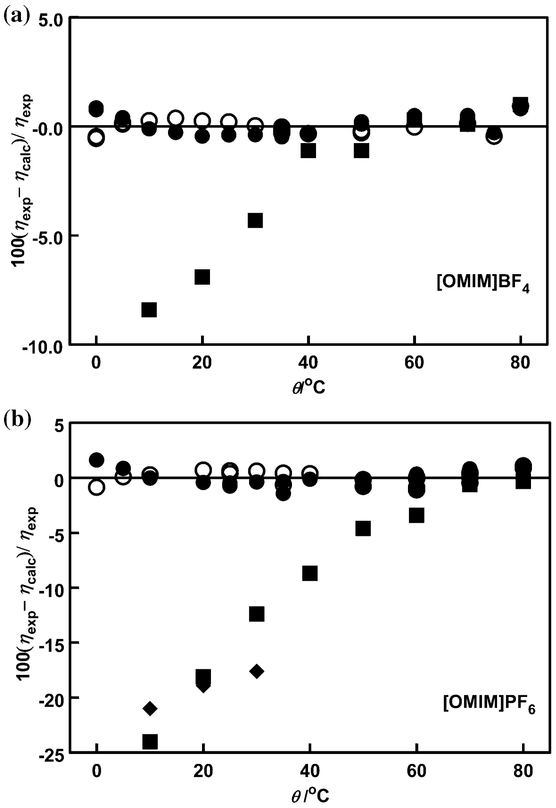

**Figure 3.** (a) Residuals (experimental − calculated values) for the fit of the experimental viscosities for [OMIM]$BF_4$ at atmospheric pressure to eqs 7 and 8 as a function of temperature, $\theta$. Symbols: ●, this work, Litovitz eq 7; ○, this work, VFT eq 8; ■, ref 11. (b) Residuals (experimental − calculated values) for the fit of the literature viscosities for [OMIM]$PF_6$ at atmospheric pressure to eqs 7 and 8 as a function of temperature, $\theta$. Symbols: ●, this work, Litovitz eq 7; ○, this work, VFT eq 8; ■, ref 11, ◆, ref 15.

**Table 8. Coefficients of Best Fit for Equations 9, 10, and 11**

| | coefficients and standard uncertainties[a] | | |
|---|---|---|---|
| | [OMIM]$BF_4$ | [OMIM]$PF_6$ | [BMIM]$PF_6$ |
| | ML, eq 9 | | |
| $a$ | $-0.4585 \pm 0.0035$ | $-0.5344 \pm 0.0062$ | $-0.4061 \pm 0.014$ |
| $b \times 10^3/\mathrm{MPa}^{-1}$ | $2.7283 \pm 0.055$ | $4.7212 \pm 0.273$ | $2.354 \pm 0.21$ |
| $c \times 10^{-6}/\mathrm{K}^3$ | $166.80 \pm 0.10$ | $189.107 \pm 0.19$ | $159.49 \pm 0.43$ |
| $d \times 10^{-6}/(\mathrm{K}^3 \cdot \mathrm{MPa}^{-1})$ | $0.2657 \pm 0.0017$ | $0.2696 \pm 0.0083$ | $0.3167 \pm 0.0068$ |
| $e/(\mathrm{K}^3 \cdot \mathrm{MPa}^{2-})$ | $-209.2 \pm 5.8$ | $-283.3 \pm 25$ | $-191.3 \pm 17$ |
| standard uncertainty of fit | 0.5 | 0.6 | 1.8 |
| | MVFT1, eq 10 | | |
| $a'$ | $-3.1947 \pm 0.030$ | $-3.5077 \pm 0.054$ | $-2.654 \pm 0.13$ |
| $b' \times 10^3/\mathrm{MPa}^{-1}$ | $-1.2181 \pm 0.079$ | $0.0742 \pm 0.\ 373$ | $-2.323 \pm 0.32$ |
| $c'/\mathrm{K}$ | $1291.0 \pm 9.2$ | $1423.6 \pm 16.4$ | $1121 \pm 37$ |
| $d'/(\mathrm{K} \cdot \mathrm{MPa}^{-1})$ | $1.991 \pm 0.013$ | $2.090 \pm 0.057$ | $2.269 \pm 0.067$ |
| $e' \times 10^5/(\mathrm{K} \cdot \mathrm{MPa}^{-2})$ | $-105.68 \pm 2.7$ | $-125.07 \pm 10.0$ | $-94.45 \pm 8.3$ |
| $T_0/\mathrm{K}$ | $155.10 \pm 0.54$ | $157.20 \pm 0.86$ | $162.2 \pm 2.4$ |
| standard uncertainty of fit | 0.5 | 0.5 | 1.8 |
| | MVFT2, eq 11 | | |
| $a''$ | $-3.234 \pm 0.032$ | $-3.4431 \pm 0.057$ | $-2.975 \pm 0.14$ |
| $b'' \times 10^3/\mathrm{MPa}^{-1}$ | $2.586 \pm 0.054$ | $4.083 \pm 0.256$ | $2.521 \pm 0.25$ |
| $D$ | $8.448 \pm 0.094$ | $8.874 \pm 0.16$ | $7.802 \pm 0.41$ |
| $x/\mathrm{K}$ | $154.322 \pm 0.56$ | $158.21 \pm 0.91$ | $156.17 \pm 2.69$ |
| $y \times 10^2/(\mathrm{K} \cdot \mathrm{MPa}^{-1})$ | $8.211 \pm 0.058$ | $8.062 \pm 0.24$ | $9.971 \pm 0.24$ |
| $z \times 10^5/(\mathrm{K} \cdot \mathrm{MPa}^{-2})$ | $-8.568 \pm 0.23$ | $-9.634 \pm 0.50$ | $-9.74 \pm 0.89$ |
| standard uncertainty of fit | 0.5 | 0.6 | 1.8 |

[a] ML and MVFT1 coefficients for [BMIM]$PF_6$ from ref 2 are included for comparison.

The negative offsets of the results of the Brennecke group[7,10] are consistent with the reported mass fractions of water in their second paper,[7] 0.0046 and 0.0024 respectively, or mole fractions 0.0675 and 0.0435. Based on our results, ideal solutions of these compositions would have densities of (1.0965 and 1.2264) $g \cdot cm^{-3}$ respectively at 25 °C. Their values are (1.0912 and 1.2245) $g \cdot cm^{-3}$. For [OMIM]$BF_4$, there is good agreement with the results of Seddon et al.,[11] who used a much drier sample ($35 \cdot 10^{-6}$ mass fraction) than the Brennecke group: there is excellent agreement at 25 °C between our result, 1.10368 $g \cdot cm^{-3}$, and that of Heintz et al.,[13] 1.10381 $g \cdot cm^{-3}$. For [OMIM]$PF_6$, there is very good agreement with the single 25 °C vibrating-tube point of Dzyuba and Bartsch.[14] The pycnometric results of Seddon et al.[11] deviate from ours in this case, but their sample contains slightly more water than ours, $80 \cdot 10^{-6}$ mass fraction.

The viscosities are presented in Table 5 and 6. As there are no high-pressure data in the literature, comparison with the results of other workers[11,15] is confined to atmospheric pressure. As for [BMIM]$PF_6$,[2] the data were fitted to the Litovitz equation:[16]

$$\eta = A \exp(B/RT^3) \tag{7}$$

which has the advantages of (a) containing only two fitted parameters and (b) being ideal for extrapolation, as well as the more commonly used Vogel−Fulcher−Tammann (VFT) equation:

$$\eta = A' \exp(B'/(T - T_0)) \tag{8}$$

The coefficients are given in Table 7. Angell[17] has developed a global classification of liquids based on eq 8. His strength parameter $D$ ($\equiv B'/T_0$) is large for “strong” liquids where the viscosity approaches an Arrhenius (Andrade) temperature dependence and is small for “fragile” liquids. A number of workers have commented on the need for care in fitting data to the VFT equation.[18] We have employed AXUM graphics software (Mathsoft Inc.) which uses the Levenberg−Marquardt nonlinear least-squares algorithm[19] recommended by Mano and Pereira,[18] fitting ln $\eta$, but weighting the data to allow for choosing this form ($w \propto 1/\eta$) and, as well, in proportion to the percentage experimental error ($w \propto \eta$). These two weightings conveniently cancel.

Figure 3 shows the deviations of our results and the literature data from these equations. When expanded to a larger scale, the residual plots show some systematic trends at the temperature extremes, but these are within the overall experimental uncertainty. The results of Seddon et al.[11] agree well with ours at higher temperatures but tend to be much lower at lower temperatures, whereas for [BMIM]$PF_6$ the results from our two groups are in better accord over the whole temperature range.[2] The results of Branco et al.[15] are also much lower, particularly for [OMIM]$BF_4$, where they are about one-third of our values. Both these data sets were obtained with cone and plate viscometers, the Branco instrument being open to the laboratory atmosphere.[20]

The general form of the pressure dependence of the shear viscosity of liquids is greater than exponential at moderate pressures [$(\partial \ln \eta/\partial p)_T < 0$] and less than exponential at very high pressures [$(\partial \ln \eta/\partial p)_T > 0$], typically above 0.5 GPa.[21,22] Consequently, as for [BMIM]$PF_6$,[2] we have used modified Litovitz (ML) and VTF (MVTF1) equations to fit the data set as a whole:

$$\eta = \exp(a + bp + (c + dp + ep^2)/T^3) \tag{9}$$

$$\eta = \exp(a' + b'p + (c' + d'p + e'p^2)/(T - T_0)) \tag{10}$$

The quality of the fits for the two equations is very similar: coefficients are given in Table 8. The modified VFT equation yields a pressure-dependent strength parameter, $D = (c' + d'p + e'p^2)/T_0$. This is plotted as a function of pressure in Figure 5 where values for [BMIM]$PF_6$ are also included. $D$ increases in the order [BMIM]$PF_6$ < [OMIM]$BF_4$ < [OMIM]$PF_6$; that is, [BMIM]$PF_6$ is the most fragile. $D$ increases with increasing pressure in each case.

It has been argued that $D$ should be independent of pressure, at least in some cases.[23,24] This then requires that $T_0$ be pressure-

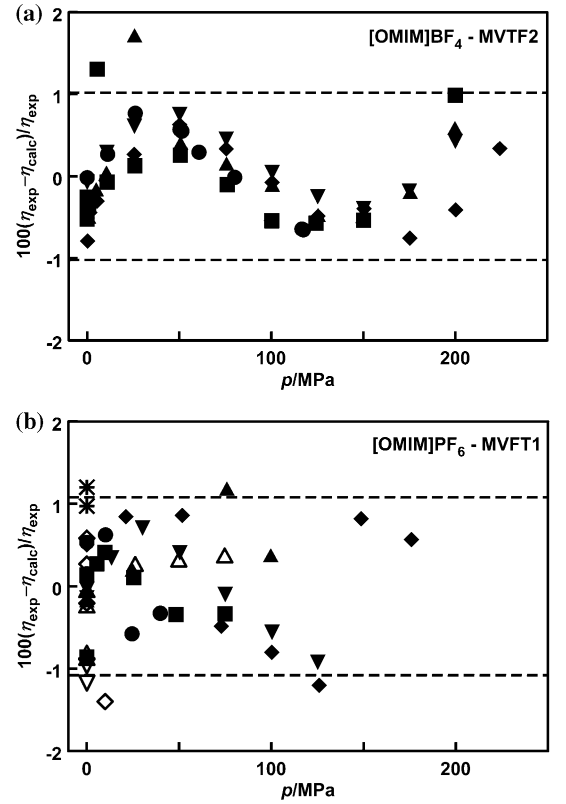

**Figure 4.** (a) Residuals (experimental − calculated values) for the fit of the experimental viscosities for [OMIM]BF$_4$ to eq 11 (MVFT2) as a function of temperature and pressure, $p$. Symbols: ●, 25 °C; ■, 35 °C; ▲, 50 °C; ▼, 60 °C; ◆, 75 °C. (b) Residuals (experimental − calculated values) for the fit of the experimental viscosities for [OMIM]PF$_6$ to eq 10 (MVFT1) as a function of temperature and pressure, $p$. Symbols: sample OP1 —, △, 50 °C; ▽, 60 °C; ◇, 70 °C; ∗80 °C; sample OP2 —, ●, 25 °C; ■, 35 °C; ▲, 50 °C; ▼, 60 °C; ◆, 70 °C.

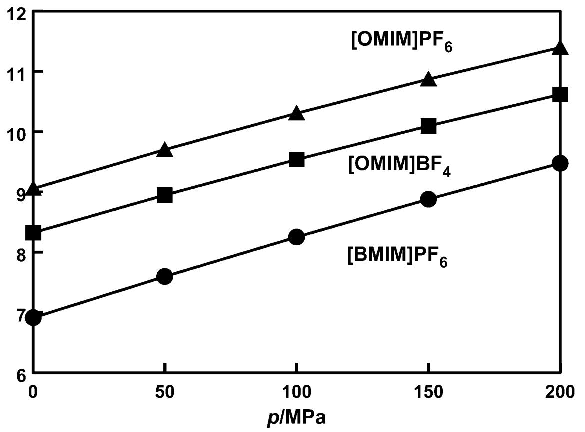

**Figure 5.** Pressure dependence of the Angell strength parameter $D$, obtained from the parameters of eq 10. Symbols: ●, [BMIM]PF$_6$; ■, [OMIM] BF$_4$; ▲, [OMIM] PF$_6$.

dependent, and it should increase with increasing pressure like the glass transition temperature, $T_g$. Accordingly, our results have also been fitted to the equation (MVFT2):

$$\eta = \exp(a'' + b''p + DT_0(p)/(T - T_0))$$

$$T_0(p) = x + yp + zp^2 \qquad (11)$$

The quality of the fit is little changed (Table 8 and Figure 4), but this is not surprising given that the number of fitted coefficients is unchanged. (It should be noted that the parameters $b'$ and $b''$ in eqs 10 and 11 seem to be necessary for an adequate fit.) Figure 6 shows that ($dT_0/dp$) is indeed positive, although it decreases slightly with increasing pressure. $T_0$ values for the two hexafluorophosphate salts are essentially equal within the error of the fits, with $T_0$ for [OMIM]BF$_4$ being slightly lower.

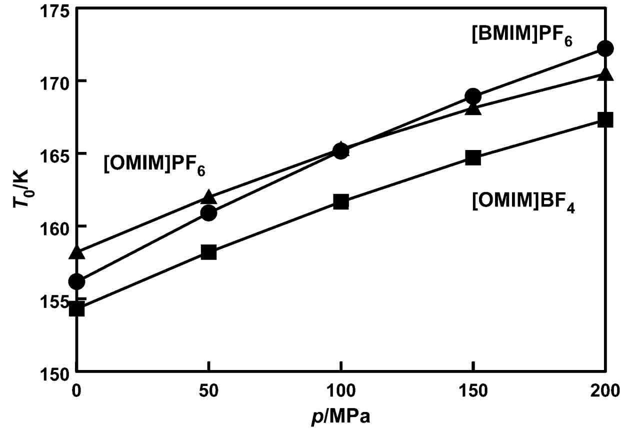

**Figure 6.** Pressure dependence of the VFT parameter $T_0$, obtained from the parameters of eq 11. Symbols are the same as for Figure 5.

**Table 9. Test of the Angell Relationship between $D$, $T_0$, and $T_g$**

| | [OMIM]BF$_4$ | [OMIM]PF$_6$ | [BMIM]PF$_6$ |
|---|---|---|---|
| | Parameters from VFT, eq 8 | | |
| $T_0$/K | 155.5 | 158.0 | 161.8 |
| $D$ | 8.25 | 8.91 | 6.96 |
| $T_g$/K$^a$ | 193.7 | 191.2 | 197.1 |
| $T_g/T_0$ | 1.25 | 1.21 | 1.22 |
| $T_g/T_0$ from eq 12 | 1.21 | 1.23 | 1.18 |
| | Parameters from MVFT2, eq 11 | | |
| $T_0(= x)$/K | 154.3 | 158.2 | 156.2 |
| $D$ | 8.45 | 8.87 | 7.80 |
| $T_g/T_0$ | 1.26 | 1.21 | 1.26 |
| $T_g/T_0$ from eq 12 | 1.22 | 1.23 | 1.20 |

[a] Glass temperatures: [OMIM]BF$_4$, ref 26; [OMIM]PF$_6$, ref 9; [BMIM]PF$_6$, ref 27.

Angell[25] has suggested the following relationship between $D$, $T_0$, and the glass temperature $T_g$, based on the scaling of the (coexistence line) viscosities of a wide range of liquids in the range $0 < (T_g/T_0) < 1$, with the assumption of a common single viscosity value ($\eta_g$) at $T_g$. Thus

$$T_g/T_0 = 1 + D/(2.303\log(\eta_g/\eta_0)) \qquad (12)$$

$\eta_0$ is $A'$ of the VFT equation (eq 8). Angell found $\log(\eta_g/\eta_0)$ empirically to be about 17. The values of $D$ and $T_0$ derived from VFT and MVFT2 and experimental $T_g$ values from the literature are found to be consistent with Angell's relationship (Table 9).

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